PESTICIDAL N-SUBSTITUTED AZACYCLIC DERIVATIVES

This application claims the benefit of U.S. Provisional Application No. 60/485,297, filed July 7, 2003.

FIELD OF THE INVENTION

The present invention relates to methods for controlling pests. In particular, it relates to control by the application of certain novel compositions containing pesticidal N-substituted azacyclic derivatives.

BACKGROUND OF THE INVENTION

It is well known that pests such as insects and acarids in general can cause significant damage, not only to crops grown in agriculture, but also, for example, to structures and turf where the damage is caused by soil-borne insects, such as termites and white grubs. Such damage may result in the loss of millions of dollars of value associated with a given crop, turf or structure. Insecticides and acaricides are useful for controlling insects and acarids which may otherwise cause significant damage to crops such as wheat, corn, soybeans, potatoes, and cotton to name a few. For crop protection, insecticides and acaricides are desired which can control the insects and acarids without damaging the crops, and which have no deleterious effects to mammals and other living organisms. Surprisingly, it has now been found that compositions of N-substituted azacyclic derivatives of the present invention are unexpectedly active in controlling sucking pests such as cotton aphids, as well as other insect species.

Pharmacologically active 1,2,4-, 1,3,4-, and 1,2,5-oxadiazoles and 1,2,4-, 1,3,4-and 1,2,5-thiadiazoles have been reported in the literature, for example, Wätjen et al., U.S. Patent No. 4,870,073; Baker et al., U.S. Patent Nos. 4,952,587 and 5,686,463 and European Patent EP 0323864 A2; Sauerberg et al., U.S. Patent Nos. 5,260,314, 5,481,240 and 5,527,813; Sauerberg et al., Journal of Medicinal Chem., Vol. 35, No. 12, pp. 2274-2283 (1992); Olesen et al., Eur. J. Med. Chem., 31, pp. 221-230 (1996); and MacLeod et al., Journal of Medicinal Chem., Vol. 33, pp. 2052-2059 (1990). Similarly, insecticidally and acaricidally active 1,2,4-, 1,3,4-, and 1,2,5-oxadiazoles, 1,2,3-, 1,2,4- and 1,3,4-thiadiazoles, 1,2,4-triazoles, and 1,2,3,4-

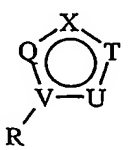
tetrazoles have been reported in the literature. For example, Dick, U.S. Patent No. 5,393,767; Tsubata et al., U.S. Patent Nos. 6,337,341 B1 and 6,348,460 B1; Theobald et al., U.S. Patent No. 4,943,584; and Matsumoto et al., U.S. Patent No. 4,722,934. EP 0445731 A1 and WO 01/15532 disclose azabicyclo and azacyclo oxime and amine compounds as pesticides. It has also been disclosed that pharmacologically active 1,2,4- and 1,2,5-thiadiazoles and insecticidally and acaricidally active 1,2,4-oxdiazoles, 1,3,4-triazoles, and 1,2,3,4-tetrazoles can act as muscarinic agonists, see, for example, Sauerberg et al., Journal of Medicinal Chem., Vol. 35, No. 12, pp. 2274-2283 (1992); Dick et al., Pestic. Sci., **49**, 268-276 (1997); Olesen et al., Eur. J. Med. Chem., 31, pp. 221-230 (1996); and MacLeod et al., Journal of Medicinal Chem., Vol. 33, pp. 2052-2059 (1990).

WO 95/03306 discloses arthropodically active substituted 1,2,5-oxadiazoles and 1,2,5-thiadiazoles; however, it specifically requires that the 1,2,5-oxadiazole or 1,2,5-thiadiazole be substituted with an azabicyclic compound rather than a tetrahydropyridyl or a pyridyl ring and that said azabicyclic compound can only attach at the two position when the bridge occurs between the nitrogen and a carbon atom on the ring.

WO 93/14636 and its equivalent U.S. Patent No. 5,244,906 disclose certain substituted 1,2,4-oxadiazoles and 1,2,4-thiadiazoles useful for control of insects, such as sucking insects like two-spotted spider mite.

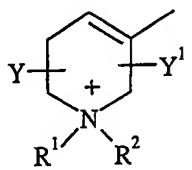
SUMMARY OF THE INVENTION

It has now been found that certain compositions containing a pesticidally effective amount of an N-substituted azacyclic derivative, and their agriculturally acceptable salts, in admixture with at least one agriculturally acceptable extender or adjuvant are surprisingly effective in controlling pests, i.e., acaricides, as well as insects. The N-substituted azacyclic derivatives may be represented by the following formula I:



wherein

-R is an azacycle selected from the following:



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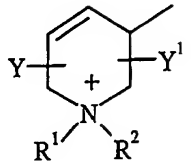

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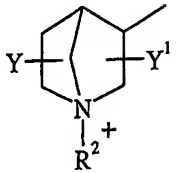

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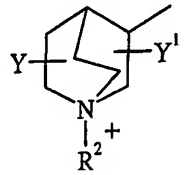

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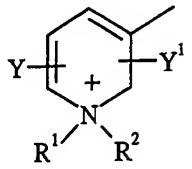

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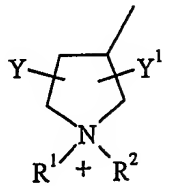

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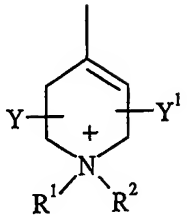

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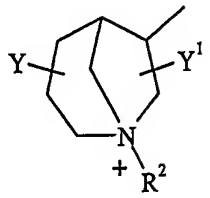

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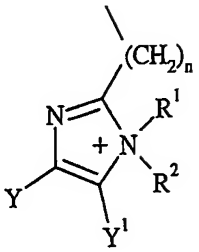

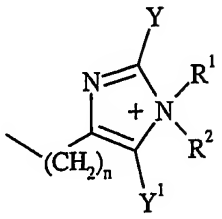

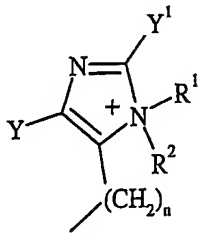

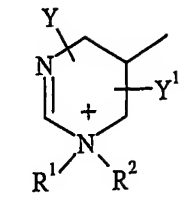

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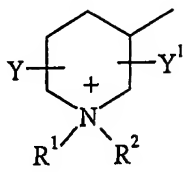

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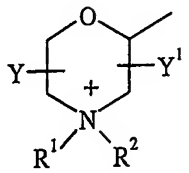

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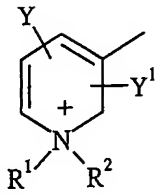

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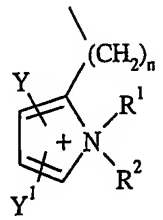

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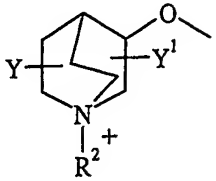

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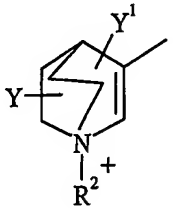

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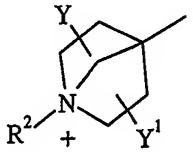

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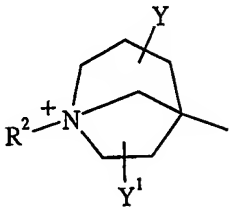

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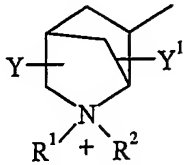

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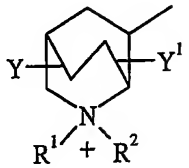

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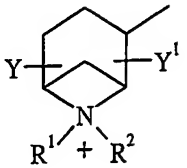

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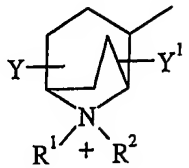

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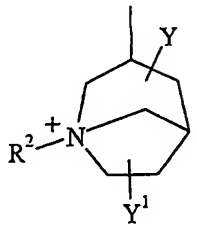

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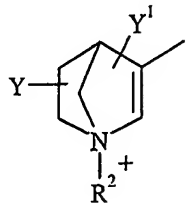

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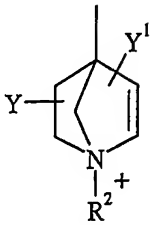

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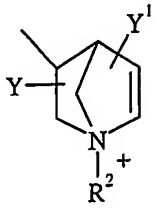

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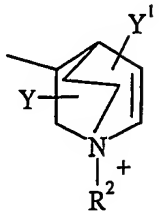

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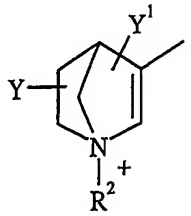

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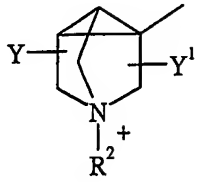

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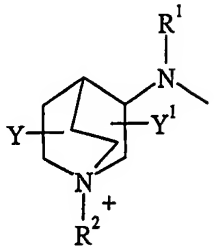

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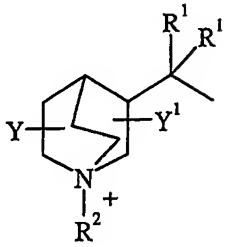

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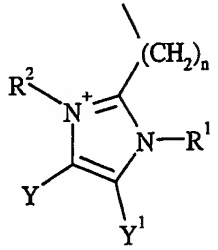

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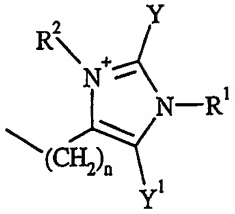

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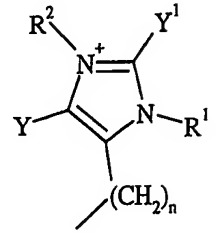

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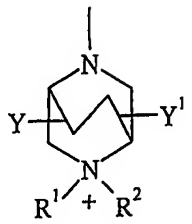

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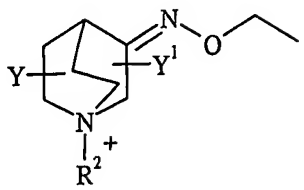

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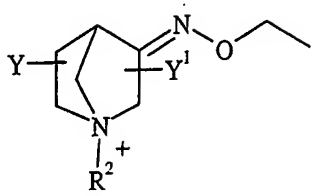

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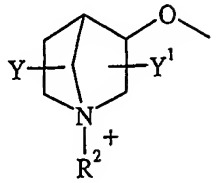


W40

where

-Y and Y^1 may be attached at the same or different positions, and are independently selected from hydrogen, halogen, hydroxy, cyano, nitro, amino, carboxyl, alkyl, haloalkyl, alkenyl, alkoxy, haloalkoxy, aminoalkoxy, alkylcarbonyl, haloalkylcarbonyl, alkoxycarbonyl, haloalkoxycarbonyl, arylalkyl, aryl, aryloxy, and heterocyclyl, where the aryl and heterocyclyl moieties may be optionally substituted with halogen, alkyl, haloalkyl, alkoxy, or haloalkoxy;

R^1 is selected from alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, arylalkyl, and aryl; wherein the aryl may be optionally substituted with halogen, alkyl, haloalkyl, alkoxy, or haloalkoxy;

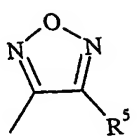
R^2 is selected from O^-, forming an N-oxide; alkyl, alkoxy, haloalkyl, alkenyl, haloalkenyl, haloalkoxy, alkylcarbonyloxy, alkoxycarbonylalkyl, ¯Ocarbonylalkyl, alkylthioalkyloxy, alkylsulfinylalkyloxy, alkylsulfonylalkyloxy, alkoxyphosphonylalkyloxy, ¯Ophosphonylalkyloxy, alkoxyalkyl, arylalkyl, arylalkyloxy, arylcarbonyloxy, arylalkoxycarbonyloxy arylalkylcarbonyloxy, aryl, -OC(O)N(R^3)(R^4); wherein the aryl may be optionally substituted with halogen, alkyl, haloalkyl, alkoxy, or haloalkoxy moiety;

where

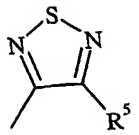
R^3 and R^4 are independently selected from hydrogen, alkyl, alkylcarbonyl, alkoxycarbonyl, alkoxyalkyl, aminoalkyl, aryl, arylalkyl, and carbonylamino; where the aryl may be optionally substituted with halogen, alkyl, haloalkyl, alkoxy, cyano, or haloalkoxy;

and,

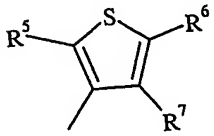
is a 5-membered heterocycle, wherein V is carbon or nitrogen; Q is carbon, nitrogen or oxygen; X is carbon, nitrogen, oxygen or sulfur, T is carbon, nitrogen, oxygen or C(=O); and U is carbon, nitrogen, oxygen or sulfur, wherein said 5-membered heterocycle is selected from the following;



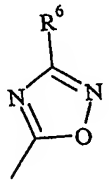
X1
a 1,2,5-oxadiazol-3-yl



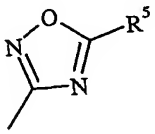
X2
a 1,2,5-thiadiazol-3-yl



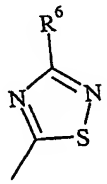
X3
a thien-3-yl



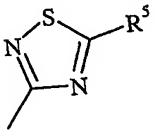
X4
a 1,2,4-oxadiazol-5-yl



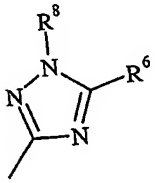
X5
a 1,2,4-oxadiazol-3-yl



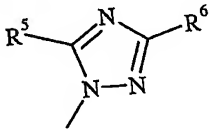
X6
a 1,2,4-thiadiazol-5-yl



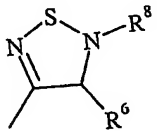
X7
a 1,2,4-thiadiazol-3-yl



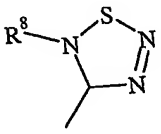
X8
a 1,2,4-triazol-3-yl



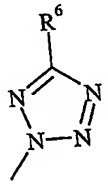
X9
a 1,2,4-triazol-1-yl



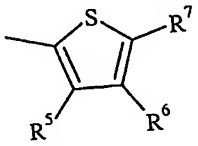
X10
a 1,2,5-thiadiazolin-3-yl



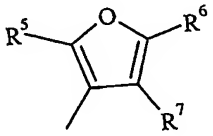
X11
a 1,2,3,5-thiatriazolin-4-yl



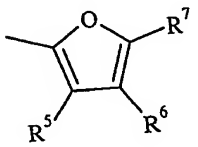
X12
a 1,2,3,4-tetraazol-2-yl



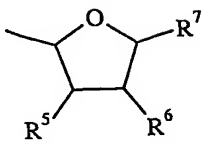
X13
a thien-2-yl



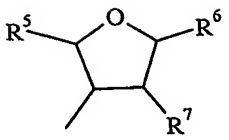
X14
a furan-3-yl



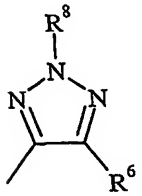
X15
a furan-2-yl



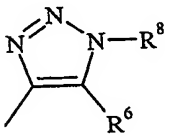
X16
a tetrahydrofuran-2-yl



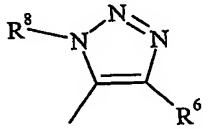
X17
a tetrahydrofuran-2-yl



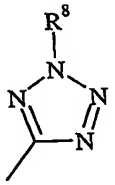
X18
a 1,2,3-triazol-4-yl



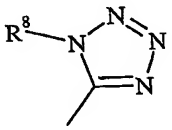
X19
a 1,2,3-triazol-4-yl



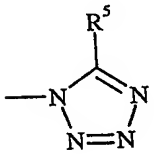
X20
a 1,2,3-triazol-4-yl



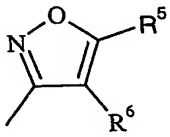
X21
a tetraazol-5-yl



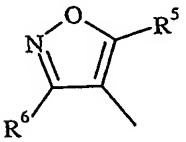
X22
a tetraazol-5-yl



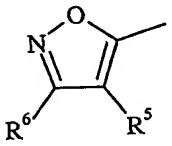
X23
a 1,2,3,4-tetraazol-1-yl



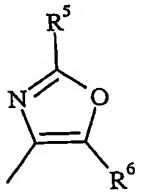
X24
an isoxazol-3-yl



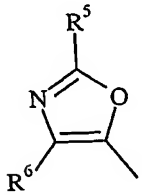
X25
an isoxazol-4-yl



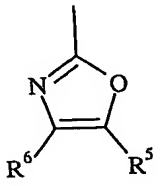
X26
an isoxazol-5-yl



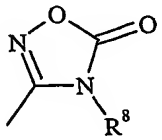
X27
a 1,3-oxazol-4-yl



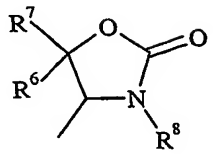
X28
an oxazol-5-yl



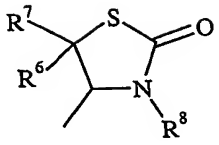
X29
an oxazol-2-yl



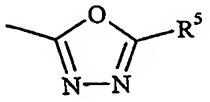
X30
a 2-oxadiazolidinon-4-yl



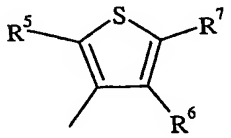
X31
a 2-oxazolidinon-4-yl



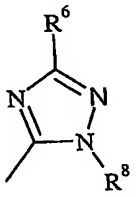
X32
a 2-thazolidinon-4-yl



X33
a 1,3,4-oxadiazol-2-yl



X34
a thien-3-yl



X35
a 1H-1,2,4-triazol-5-yl

where

-R^5, R^6 and R^7 are independently selected from hydrogen; hydroxy; hydroxyalkyl, aminoalkyl, halogen; amino; nitro; alkynyl; haloalkynyl; alkoxy; alkoxyalkyl, haloalkoxy; aryl, arylalkyloxy, alkenyloxy; alkynyloxy; thiol; alkylthio; haloalkylthio; cyanoalkylthio; alkenylthio; alkynylthio; alkoxythio, carboxyl, formyl; alkyloxycarbonyl; carboxyl; $-N(R^9)(R^{10})$; $-NHN(R^9)(R^{10})$; $-NHC(O)R^9$; $-NHC(O)OR^9$; $-OC(O)R^9$; where the aryl may be optionally substituted with halogen, alkyl, haloalkyl, alkoxy, cyano, or haloalkoxy;

where

R^8 is selected from alkyl, haloalkyl, arylalkyl, alkoxy, alkenyl, haloalkenyl, alkynyl, haloalkynyl,

where

R^9 and R^{10} are independently selected from hydrogen, alkyl, alkenyl, alkynyl, alkylthio, alkylcarbonyl, alkoxycarbonyl, aryl, arylalkyl, and carbonylamino; where the aryl may be optionally substituted with halogen, alkyl, haloalkyl, alkoxy, cyano, or haloalkoxy;

and

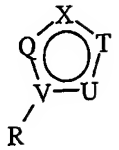
the corresponding agriculturally acceptable salts thereof.

The present invention is also directed to methods of controlling pests, such as insects and acarids, where control is desired, which comprises applying a pesticidally

effective amount of the above composition to a locus of crops, or other areas where pests are present or are expected to be present.

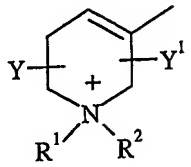
DETAILED DESCRIPTION OF THE INVENTION

In one aspect, the present invention relates to compositions containing a pesticidally effective amount of an N-substituted azacyclic derivative and their agriculturally acceptable salts, in admixture with at least one agriculturally acceptable extender or adjuvant which are surprisingly effective as pesticides, i.e., as acaricides and insecticides. Generally, the N-substituted azacyclic derivatives may be represented by the following formula I:

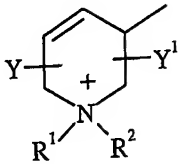


wherein

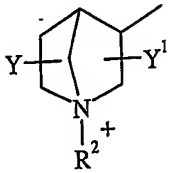
-R is an azacycle selected from the following:



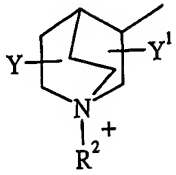
W1



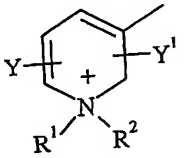
W2



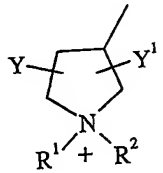
W3



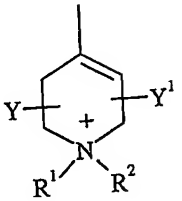
W4



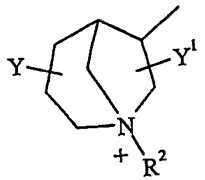
W5



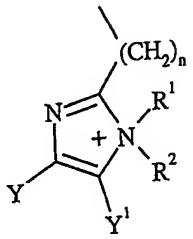
W6



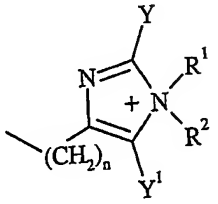
W7



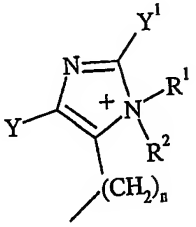
W8



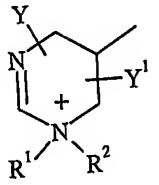
W9



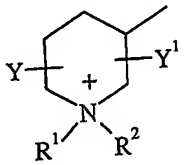
W10



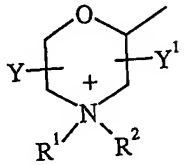
W11



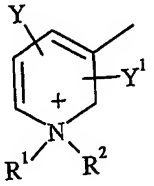
W12



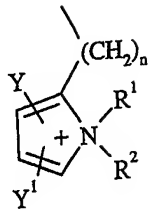
W13



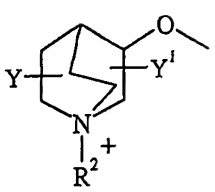
W14



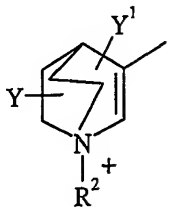
W15



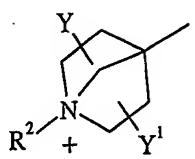
W16



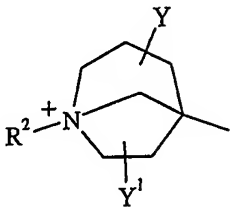
W17



W18



W19



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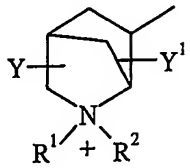
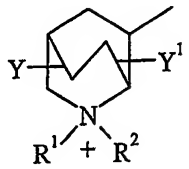
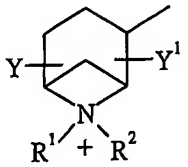


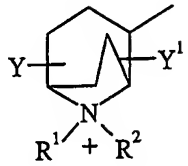
W21



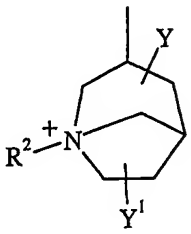
W22



W23



W24



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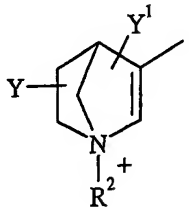
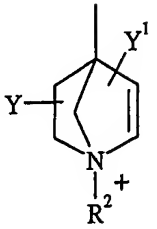
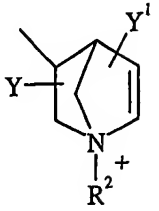


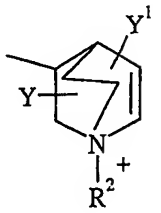
W26



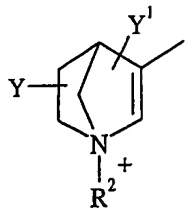
W27



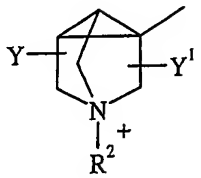
W28



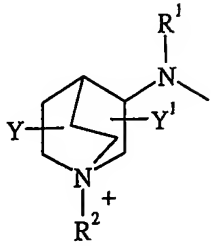
W29



W30



W31



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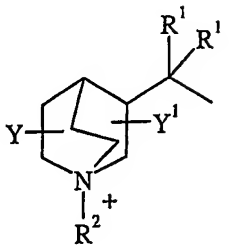
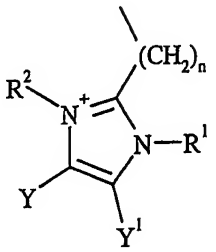


W33



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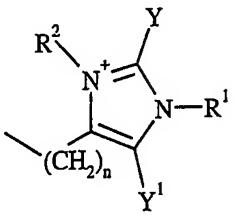
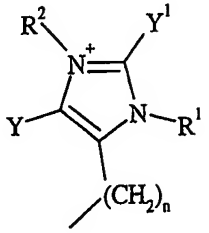
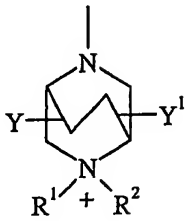


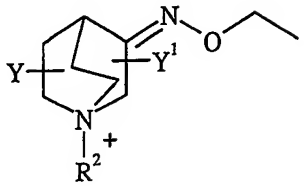
W35



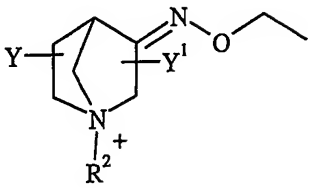
W36



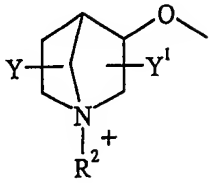
W37



W38



W39



W40

where

-Y and Y^1 may be attached at the same or different positions, and are independently selected from hydrogen, halogen, hydroxy, cyano, nitro, amino, carboxyl, alkyl, haloalkyl, alkenyl, alkoxy, haloalkoxy, aminoalkoxy, alkylcarbonyl, haloalkylcarbonyl, alkoxycarbonyl, haloalkoxycarbonyl, arylalkyl, aryl, aryloxy, and heterocyclyl, where the aryl and heterocyclyl moieties may be optionally substituted with halogen, alkyl, haloalkyl, alkoxy, or haloalkoxy;

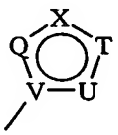
R^1 is selected from alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, arylalkyl, and aryl; wherein the aryl may be optionally substituted with halogen, alkyl, haloalkyl, alkoxy, or haloalkoxy;

R^2 is selected from O^-, forming an N-oxide; alkyl, alkoxy, haloalkyl, alkenyl, haloalkenyl, haloalkoxy, alkylcarbonyloxy, alkoxycarbonylalkyl, Ocarbonylalkyl, alkylthioalkyloxy, alkylsulfinylalkyloxy, alkylsulfonylalkyloxy, alkoxyphosphonylalkyloxy, Ophosphonylalkyloxy, alkoxyalkyl, arylalkyl, arylalkyloxy, arylcarbonyloxy, arylalkoxycarbonyloxy arylalkylcarbonyloxy, aryl, $-OC(O)N(R^3)(R^4)$; wherein the aryl may be optionally substituted with halogen, alkyl, haloalkyl, alkoxy, or haloalkoxy moiety;

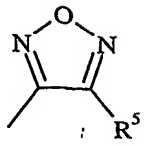
where

R^3 and R^4 are independently selected from hydrogen, alkyl, alkylcarbonyl, alkoxycarbonyl, alkoxyalkyl, aminoalkyl, aryl, arylalkyl, and carbonylamino; where the aryl may be optionally substituted with halogen, alkyl, haloalkyl, alkoxy, cyano, or haloalkoxy;

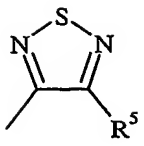
and,



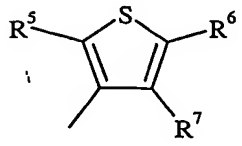
is a 5-membered heterocycle, wherein V is carbon or nitrogen; Q is carbon, nitrogen or oxygen; X is carbon, nitrogen, oxygen or sulfur, T is carbon, nitrogen, oxygen or C(=O); and U is carbon, nitrogen, oxygen or sulfur, wherein said 5-membered heterocycle is selected from the following;



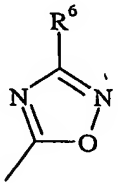
X1
a 1,2,5-oxadiazol-3-yl



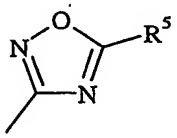
X2
a 1,2,5-thiadiazol-3-yl



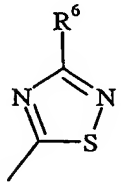
X3
a thien-3-yl



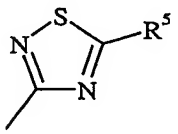
X4
a 1,2,4-oxadiazol-5-yl



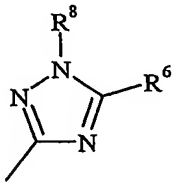
X5
a 1,2,4-oxadiazol-3-yl



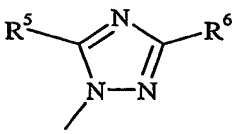
X6
a 1,2,4-thiadiazol-5-yl



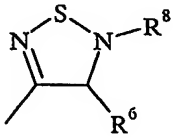
X7
a 1,2,4-thiadiazol-3-yl



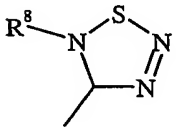
X8
a 1,2,4-triazol-3-yl



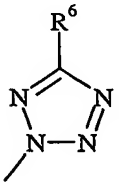
X9
a 1,2,4-triazol-1-yl



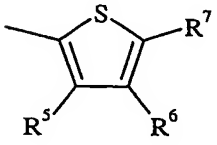
X10
a 1,2,5-thiadiazolin-3-yl



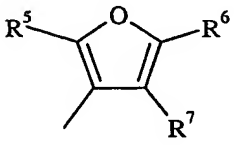
X11
a 1,2,3,5-thiatriazolin-4-yl



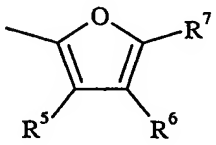
X12
a 1,2,3,4-tetraazol-2-yl



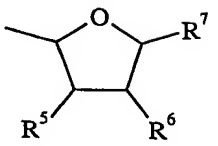
X13
a thien-2-yl



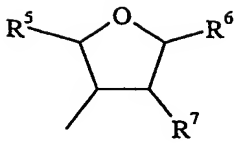
X14
a furan-3-yl



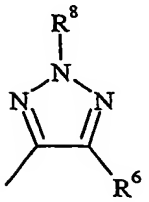
X15
a furan-2-yl



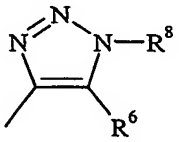
X16
a tetrahydrofuran-2-yl



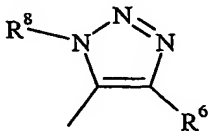
X17
a tetrahydrofuran-2-yl



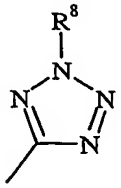
X18
a 1,2,3-triazol-4-yl



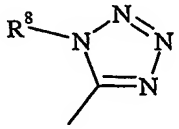
X19
a 1,2,3-triazol-4-yl



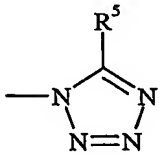
X20
a 1,2,3-triazol-4-yl



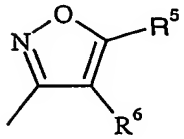
X21
a tetraazol-5-yl



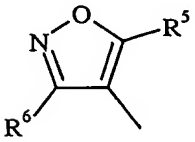
X22
a tetraazol-5-yl



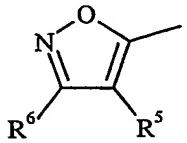
X23
a 1,2,3,4-tetraazol-1-yl



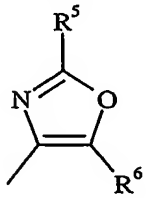
X24
an isoxazol-3-yl



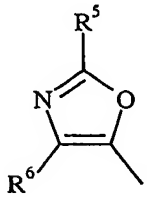
X25
an isoxazol-4-yl



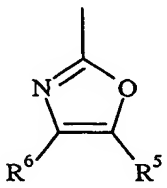
X26
an isoxazol-5-yl



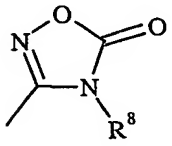
X27
a 1,3-oxazol-4-yl



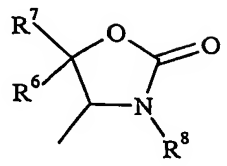
X28
an oxazol-5-yl



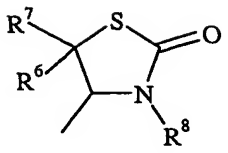
X29
an oxazol-2-yl



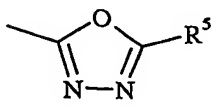
X30
a 2-oxadiazolidinon-4-yl



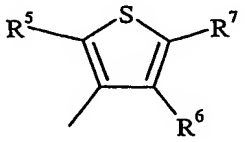
X31
a 2-oxazolidinon-4-yl



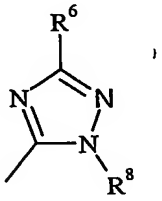
X32
a 2-thazolidinon-4-yl



X33
a 1,3,4-oxadiazol-2-yl



X34
a thien-3-yl



X35
a 1H-1,2,4-triazol-5-yl

where

-R^5, R^6 and R^7 are independently selected from hydrogen; hydroxy; hydroxyalkyl, aminoalkyl, halogen; amino; nitro; alkynyl; haloalkynyl; alkoxy; alkoxyalkyl, haloalkoxy; aryl, arylalkyloxy, alkenyloxy; alkynyloxy; thiol; alkylthio; haloalkylthio; cyanoalkylthio; alkenylthio; alkynylthio; alkoxythio, carboxyl, formyl; alkyloxycarbonyl; carboxyl; -$N(R^9)(R^{10})$; -$NHN(R^9)(R^{10})$; -$NHC(O)R^9$; -$NHC(O)OR^9$; -$OC(O)R^9$; where the aryl may be optionally substituted with halogen, alkyl, haloalkyl, alkoxy, cyano, or haloalkoxy;

where

R^8 is selected from alkyl, haloalkyl, arylalkyl, alkoxy, alkenyl, haloalkenyl, alkynyl, haloalkynyl,

where

R^9 and R^{10} are independently selected from hydrogen, alkyl, alkenyl, alkynyl, alkylthio, alkylcarbonyl, alkoxycarbonyl, aryl, arylalkyl, and carbonylamino; where the aryl may be optionally substituted with halogen, alkyl, haloalkyl, alkoxy, cyano, or haloalkoxy;

and

the corresponding agriculturally acceptable salts thereof.

Agriculturally acceptable salts of the N-substituted azacyclic derivatives of the present invention include, without limitation, iodide and bromide salts and the

salts of hydrochloric acid, hydrobromic acid, hydroiodic acid, ethanesulfonic acid, trifluoroacetic acid, methylbenzenesulfonic acid, phosphoric acid, gluconic acid, pamoic acid, and carboxylic acid.

Preferred compositions comprised of the N-substituted azacyclic derivatives of the present invention, selected from those set forth above, are those where R is selected from W1, W3, W4, W8, W13 and W20;

-Y and Y^1 are independently selected from hydrogen and halogen;

-R^1 is selected from alkyl, haloalkyl, alkoxyalkyl, arylalkyl, alkenyl, haloalkenyl and alkynyl,

and

-R^2 is O^-; forming an N-oxide;

and

the 5-membered heterocyle is selected from X2, X4, X6, X8, X12, X18, X33 and X34;

where

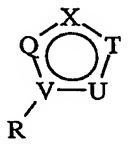
-R^5, R^6 and R^7 are independently selected from hydrogen; halogen; amino; alkyl, alkenyloxy, haloalkenyloxy, alkynyloxy, haloalkynyloxy, alkoxy, and haloalkoxy.

More preferred compositions comprised of N-substituted azacyclic derivatives of the present invention, selected from those set forth above, are those where the azacycle R is selected from W1, W3, W4, W8 and W20; Y and Y^1 are hydrogen; R^1 is selected from methyl and ethyl, and the 5-membered heterocyle is selected i) from X2 where R^5 is hydrogen and X6 where R^6 is hydrogen; ii) from X4 and X12, where R^6 is selected from halogen, alkyl and amino; iii) from X8, where R^6 is hydrogen and R^8 is selected from alkyl and arylalkyl; iv) from X18, where R^8 is alkyl; and v) from X34, where R^5 is hydrogen and R^6 is alkoxy.

Yet more preferred compositions comprised of the N-substituted azacyclic derivatives are those compositions where the 5-membered heterocyle is selected i) from X2; ii) from X4, where R^6 is methyl or ethyl; and iii) from X12, where R^6 is methyl; and even more preferred are those the azacycle R is W3 and the 5-membered heterocyle is selected i) from X4, where R^6 is methyl; and ii) from X12.

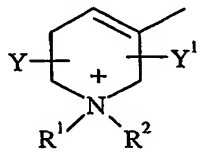
More specifically, compositions comprising a pesticidally effective amount of an N-substituted azacyclic derivative and their agriculturally acceptable salts, in

admixture with at least one agriculturally acceptable extender or adjuvant are surprisingly effective as pesticides, i.e., as acaricides and insecticides. The N-substituted azacyclic derivatives may be represented by the following formula I:

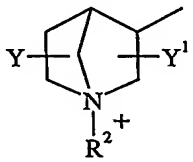


wherein

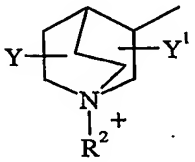
-R is an azacycle selected from the following:



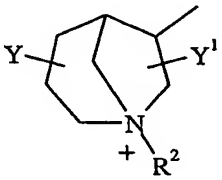
W1



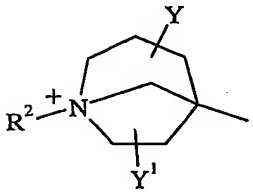
W3



W4



W8



W20

where

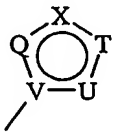
-Y and Y^1 may be attached at the same or different positions, and are independently selected from hydrogen and halogen;

-R^1 is selected from alkyl, haloalkyl, alkoxyalkyl, arylalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl,

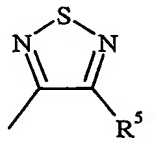
and

-R^2 is O^-; forming an N-oxide;

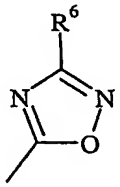
and



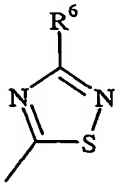
is a 5-membered heterocycle, wherein V is carbon or nitrogen; Q is carbon or nitrogen; X is carbon, nitrogen or sulfur, T is carbon or nitrogen; and U is carbon, nitrogen, oxygen or sulfur, wherein the 5-membered heterocycle is selected from the following;



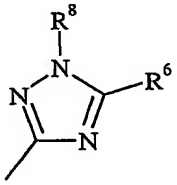
X2
a 1,2,5-thiadiazol-3-yl



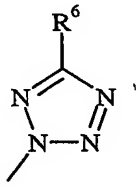
X4
a 1,2,4-oxadiazol-5-yl



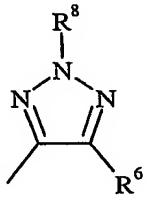
X6
a 1,2,4-thiadiazol-5-yl



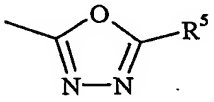
X8
a 1,2,4-triazol-3-yl



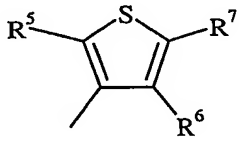
X12
a 1,2,3,4-tetraazol-2-yl



X18
a 1,2,3-triazol-4-yl



X33
a 1,3,4-oxadiazol-2-yl



X34
a thien-3-yl

where

-R^5, R^6 and R^7 are independently selected from hydrogen; halogen; amino; alkyl, alkoxy, alkenyloxy, and alkynyloxy;

and

the corresponding agriculturally acceptable salts thereof.

Preferred compositions comprised of the N-substituted azacyclic derivatives of the present invention, selected from those set forth above, are those where Y and Y^1 are hydrogen; R^1 is selected from methyl and ethyl and the 5-membered

heterocyle is selected i) from X2 where R^5 is hydrogen and X6 where R^6 is hydrogen; ii) from X4 and X12, where R^6 is selected from halogen, alkyl and amino; iii) from X8, where R^6 is hydrogen and R^8 is selected from alkyl and arylalkyl; iv) from X18, where R^8 is alkyl; and v) from X34, where R^5 is hydrogen and R^6 is alkoxy.

More preferred compositions comprised of the N-substituted azacyclic derivatives of the present invention, selected from those set forth above, are those where the 5-membered heterocyle is selected i) from X2; ii) from X4, where R^6 is methyl or ethyl; and iii) from X12, where R^6 is methyl; and especially preferred are those compositions wherein the azacycle R is W3 and the 5-membered heterocyle is selected i) from X4, where R^6 is methyl; and ii) from X12.

As used in this specification and unless otherwise indicated, the substituent terms "alkyl" and "alkoxy", alone or as part of a larger moiety, include chains of 1 to 14 carbon atoms, preferably straight or branched alkyls of 1 to 6 carbon atoms; while "halogen" or "halo", alone or as part of a larger moiety, includes chlorine, bromine, fluorine, and iodine atoms. The terms "alkenyl" or "alkynyl", used alone or as part of a larger moiety, includes straight or branched chains of at least two carbon atoms containing at least one carbon-carbon double or triple bond, preferably up to 12 carbon atoms, more preferably, up to ten carbon atoms, most preferably up to seven carbon atoms. The term "cycloalkyl" includes rings of three to twelve carbon atoms, preferably rings of three to six carbon atoms. The terms "haloalkyl" and "haloalkoxy", alone or as part of a larger moiety, include straight or branched chain alkyls of 1 to 14 carbon atoms, preferably lower straight or branched chain alkyls of 1 to 6 carbon atoms, wherein one or more hydrogen atoms have been replaced with halogen atoms, as, for example, trifluoromethyl or 2,2,2-trifluoroethoxy, respectively. "Aryl" refers to an aromatic ring structure, including fused rings, having 5 to 10 carbon atoms. "Heterocyclyl" refers to an aromatic ring structure, including fused rings, having at least one nitrogen, sulfur or oxygen atom. "Amino" refers to compounds of nitrogen that may be considered derived from ammonia and includes primary, secondary and tertiary amines wherein one or more of the hydrogen atoms is replaced with alkyl groups. "THF" refers to tetrahydrofuran, "DMF" refers to N,N-dimethylformamide, "MeOH" refers to methanol, "EtOH"

refers to ethanol, "DMAC" refers to N,N-dimethylacetamide, and "TEA" refers to triethylamine.

The term 'pesticide" or 'pesticidal" refers to insecticide, acaricide or insecticidal and acaricidal, respectively.

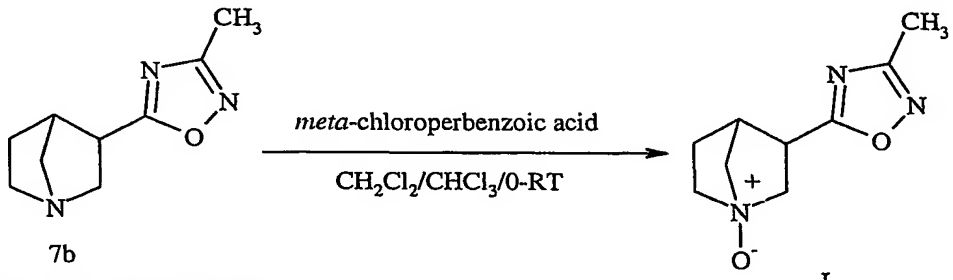
The term "pesticidally effective amount" refers to an insecticidally effective amount and an acaricidally effective amount, and as used in the context of the present invention, refers to a rate of application of a compound of the present invention applied to a locus where insect and acarid control is needed. Such a pesticidally effective amount in the context of the present invention is in the range of 10ppm to 1000ppm. Of course, one skilled in the art will realize that the pesticidally effective amount may not be the same to control both insects and acarids.

The term "translaminar" as it relates to the present invention refers to the physical ability of a pesticide to enter a plant such as a crop plant through the outer surface of its leaves or through its root system, thereby becoming a presence within the plants' circulatory system. Pesticides, for example insecticides and acaricides that are translaminar may offer an advantage in that they are longer lasting because they are protected within the plant from such deleterious effects as caused by sunlight and rain washoff. Hence, insecticides and acaricides that are translaminar may provide long term residual insecticidal and acaricidal activity. In addition, translaminar insecticides and acaricides are particularly suited for the control of piercing, sucking pests that feed on saps and juices in the plant.

The compounds of the present invention may be synthesized by methods that are individually known to those skilled in the art from intermediate compounds readily available in commerce. As set forth in the preparative examples below, many of the intermediates penultimate to the N-substituted azacyclic derivatives of the present invention are known compounds synthetically prepared in specific references. For example the intermediate penultimate to Compound 6 (Example 2 below) is compound 11 in *J. Med. Chem*, 1992, *35*, 2274-2283. The intermediate penultimate to Compound 396 (Example 3 below) is compound 7b in *J. Med. Chem*, 1991, *34*, 2726-2735. The intermediate penultimate to Compound 402 (Example 1 below) is compound 2o in *J. Med. Chem*, 1992, *35*, 2392-2406. The intermediate penultimate to Compound 407 (Example 4 below) is compound 28 in *J. Med. Chem*,

1992, *35*, 1280-1290. The intermediate penultimate to Compound 685 (Example 6 below) is compound 9b in *J. Med. Chem*, 1991, *34*, 2726-2735. The penultimate intermediates set forth above were converted to the compounds of formula I of the present invention also by methods known to one skilled in the art. The scheme below sets forth one such method:

Scheme 1



7b I

J. Med. Chem, 1991, *34*, 2726-2735

As depicted in Scheme 1 the known compound 7b was oxidized using meta-chloroperbenzoic acid, yielding a compound of formula I.

The compositions of the present invention are those compositions that are normally employed in the art for facilitating the dispersion of active ingredients for the particular utility desired, recognizing the fact that the composition and mode of application of a toxicant may affect the activity of the material in a given application. Thus, for agricultural use the present pesticidal, i.e., insecticidal and acaricidal compositions may be granules of relatively large particle size, water-soluble or water-dispersible granules, powdery dusts, wettable powders, emulsifiable concentrates, solutions, or as any of several other known types of compositions, depending on the desired mode of application.

These insecticidal and acaricidal compositions may be applied either as water-diluted sprays, or dusts, or granules to the areas in which insect and arachnid control is desired. These compositions may contain as little as 0.1%, 0.2% or 0.5% to as much as 95% or more by weight of active ingredient.

Dusts are free flowing admixtures of the active ingredients with finely divided solids such as talc, natural clays, kieselguhr, flours such as walnut shell and cottonseed flours, and other organic and inorganic solids which act as dispersants and carriers for the toxicant; these finely divided solids have an average particle size

of less than about 50 microns. A typical dust composition useful herein is one containing 1.0 part or less of the insecticidal and acaricidal compound and 99.0 parts of talc.

Wettable powders are in the form of finely divided particles which disperse readily in water or other dispersant. The wettable powder is ultimately applied to the locus where insect and arachnid control is desired either as a dry dust or as an emulsion in water or other liquid. Typical carriers for wettable powders include Fuller's earth, kaolin clays, silicas, and other highly absorbent, readily wet, inorganic diluents. Wettable powders normally are prepared to contain about 5-80% of active ingredient, depending on the absorbency of the carrier, and usually also contain a small amount of a wetting, dispersing, or emulsifying agent to facilitate dispersion. For example, a useful wettable powder composition contains 80.8 parts of the insecticidal and acaricidal compound, 17.9 parts of Palmetto clay, and 1.0 part of sodium lignosulfonate and 0.3 part of sulfonated aliphatic polyester as wetting agents.

Other useful compositions for insecticidal and acaricidal applications are emulsifiable concentrates (ECs) which are homogeneous liquid compositions dispersible in water or other dispersant, and may consist entirely of the insecticidal and acaricidal compound and a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthas, isophorone, or other non-volatile organic solvent. For insecticidal and acaricidal application these concentrates are dispersed in water or other liquid carrier, and normally applied as a spray to the area to be treated. The percentage by weight of the essential active ingredient may vary according to the manner in which the composition is to be applied, but in general comprises 0.5 to 95% of active ingredient by weight of the insecticidal and acaricidal composition.

Flowable compositions are similar to ECs except that the active ingredient is suspended in a liquid carrier, generally water. Flowables, like ECs, may include a small amount of a surfactant, and contain active ingredient in the range of 0.5 to 95%, frequently from 10 to 50%, by weight of the composition. For application, flowables may be diluted in water or other liquid vehicle, and are normally applied as a spray to the area to be treated.

Typical wetting, dispersing, or emulsifying agents used in agricultural compositions include, but are not limited to, the alkyl and alkylaryl sulfonates and sulfates and their sodium salts; alkylaryl polyether alcohols; sulfated higher alcohols; polyethylene oxides; sulfonated animal and vegetable oils; sulfonated petroleum oils; fatty acid esters of polyhydric alcohols and the ethylene oxide addition products of such esters; and the addition product of long-chain mercaptans and ethylene oxide. Many other types of useful surface-active agents are available in commerce. The surface-active agents, when used, normally comprise from 1 to 15% by weight of the composition.

Other useful compositions include suspensions of the active ingredient in a relatively non-volatile solvent such as water, corn oil, kerosene, propylene glycol, or other suitable solvents.

Still other useful compositions for insecticidal and acaricidal applications include simple solutions of the active ingredient in a solvent in which it is completely soluble at the desired concentration, such as acetone, alkylated naphthalenes, xylene, or other organic solvents. Granular compositions, wherein the toxicant is carried on relatively coarse particles, are of particular utility for aerial distribution or for penetration of cover crop canopy. Pressurized sprays, typically aerosols wherein the active ingredient is dispersed in finely divided form as a result of vaporization of a low boiling dispersant solvent carrier, such as carbon dioxide, propane, or butane, may also be used. Water-soluble or water-dispersible granules are also useful compositions for insecticidal and acaricidal application of the present compounds. Such granular compositions are free-flowing, non-dusty, and readily water-soluble or water-miscible. The soluble or dispersible granular compositions described in U.S. Pat. No. 3,920,442 are useful herein with the present insecticidal and acaricidal compounds. In use by the farmer on the field, the granular compositions, emulsifiable concentrates, flowable concentrates, solutions, etc., may be diluted with water to give a concentration of active ingredient in the range of say 0. 1% or 0.2% to 1.5% or 2%.

The active insecticidal compounds of this invention may be formulated and/or applied with one or more second compounds. Second compounds include, but are not limited to, other pesticides, plant growth regulators, fertilizers, soil

conditioners, or other agricultural chemicals. In applying an active compound of this invention, whether formulated alone or with other agricultural chemicals, an effective amount and concentration of the active compound is of course employed; the amount may vary in the range of, e.g. about 0.02 to about 1.5kg/ha, preferably about 0.05 to about 0.3 kg/ha. For field use, where there are losses of insecticide, higher application rates (e.g., four times the rates mentioned above) may be employed.

When the active pesticidal compounds of the present invention are used in combination with one or more of second compounds, e.g., with other pesticides such as herbicides, the herbicides include, without limitation, for example: N-(phosphonomethyl)glycine ("glyphosate"); aryloxyalkanoic acids such as (2,4-dichlorophenoxy)acetic acid ("2,4-D"), (4-chloro-2-methylphenoxy)acetic acid ("MCPA"), (+/-)-2-(4chloro-2-methylphenoxy)propanoic acid ("MCPP"); ureas such as N,N-dimethyl-N'-[4-(1-methylethyl)phenyl]urea ("isoproturon"); imidazolinones such as 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-pyridinecarboxylic acid ("imazapyr"), a reaction product comprising (+/-)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-4-methylbenzoic acid and (+/-)2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-methylbenzoic acid ("imazamethabenz"), (+/-)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-ethyl-3-pyridinecarboxylic acid ("imazethapyr"), and (+/-)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid ("imazaquin"); diphenyl ethers such as 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid ("acifluorfen"), methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate ("bifenox"), and 5-[2-chloro-4-(trifluoromethyl)phenoxy]-N-(methylsulfonyl)-2-nitrobenzamide ("fomasafen"); hydroxybenzonitriles such as 4-hydroxy-3,5-diiodobenzonitrile ("ioxynil") and 3,5-dibromo-4-hydroxybenzonitrile ("bromoxynil"); sulfonylureas such as 2-[[[[(4chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoic acid ("chlorimuron"), 2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide (achlorsulfuron"), 2-[[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sufonyl]methyl]benzoic acid ("bensulfuron"), 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-methy-1H-

pyrazol-4-carboxylic acid ("pyrazosulfuron"), 3-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylic acid ("thifensulfuron"), and 2-(2-chloroethoxy)-N[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide ("triasulfuron"); 2-(4-aryloxy-phenoxy)alkanoic acids such as (+/-)-2[4-[(6-chloro-2-benzoxazolyl)oxy]phenoxy]-propanoic acid (fenoxaprop"), (+/-)-2-[4[[5-(trifluoromethyl)-2-pyridinyl]oxy]-phenoxy]propanoic acid ("fluazifop"), (+/-)-2-[4-(6chloro-2-quinoxalinyl)oxy]-phenoxy]propanoic acid ("quizalofop"), and (+ /-) -2-[(2,4-dichlorophenoxy)phenoxy]propanoic acid ("diclofop"); benzothiadiazinones such as 3-(1-methylethyl)-1H-1,2,3-benzothiadiazin-4(3H)-one-2,2-dioxide ("bentazone"); 2-chloroacetanilides such as N-(butoxymethyl)-2-chloro-N-(2,6-diethylphenyl)acetamide ("butachlor"), 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide ("metolachlor"), 2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide ("acetochlor"), and (*RS*)-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)acetamide ("dimethenamide"); arenecarboxylic acids such as 3,6-dichloro-2-methoxybenzoic acid ("dicamba"); pyridyloxyacetic acids such as [(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid ("fluroxypyr"), and other herbicides.

When the active pesticidal compounds of the present invention are used in combination with one or more of second compounds, e.g., with other pesticides such as other insecticides, the other insecticides include, for example: organophosphate insecticides, such as chlorpyrifos, diazinon, dimethoate, malathion, parathion-methyl, and terbufos; pyrethroid and non-pyrethroid insecticides, such as fenvalerate, deltamethrin, fenpropathrin, cyfluthrin, flucythrinate, *alpha*-cypermethrin, bifenthrin, cypermethrin, resolved cyhalothrin, etofenprox, esfenvalerate, tralomethrin, tefluthrin, cycloprothrin, betacyfluthrin, acrinathrin and silafluofen; carbamate insecticides, such as aldicarb, carbaryl, carbofuran, and methomyl; organochlorine insecticides, such as endosulfan, endrin, heptachlor, and lindane; benzoylurea insecticides, such as diflubenuron, triflumuron, teflubenzuron, chlorfluazuron, flucycloxuron, hexaflumuron, noviflumuron, flufenoxuron, and lufenuron; and other insecticides, such as, without limitation, amitraz, clofentezine, fenpyroximate, hexythiazox, cyhexatin, spinosad, imidacloprid, chlorfenaptr,

hydramethylon, acequinocyl, fenbutatin-oxide, methoxyfenozide, tebufenozide, halofenozide, indoxacarb, fipronyl, ethiprole, etoxazole, bifenazate, spirodiclofen, spiromesifen, methoprene, pyriproxyfen, fenoxycarb, pymetrozine, abamectin, emamectin benzoate, milbemectin, and other insecticides.

When the active pesticidal compounds of the present invention are used in combination with one or more of second compounds, e.g., with other pesticides such as fungicides, the fungicides include, for example: benzimidazole fungicides, such as benomyl, carbendazim, thiabendazole, and thiophanate-methyl; 1,2,4-triazole fungicides, such as epoxyconazole, cyproconazole, flusilazole, flutriafol, propiconazole, tebuconazole, triadimefon, and triadimenol; substituted anilide fungicides, such as metalaxyl, oxadixyl, procymidone, and vinclozolin; organophosphorus fungicides, such as fosetyl, iprobenfos, pyrazophos, edifenphos, and tolclofos-methyl; morpholine fungicides, such as fenpropimorph, tridemorph, and dodemorph; other systemic fungicides, such as fenarimol, imazalil, prochloraz, tricyclazole, and triforine; dithiocarbamate fungicides, such as mancozeb, maneb, propineb, zineb, and ziram; non-systemic fungicides, such as chlorothalonil, dichlofluanid, dithianon, and iprodione, captan, dinocap, dodine, fluazinam, gluazatine, PCNB, pencycuron, quintozene, tricylamide, and validamycin; inorganic fungicides, such as copper and sulphur products, and other fungicides.

When the active pesticidal compounds of the present invention are used in combination with one or more of second compounds, e.g., with other pesticides such as nematicides, the nematicides include, for example: carbofuran, carbosulfan, turbufos, aldecarb, ethoprop, fenamphos, oxamyl, isazofos, cadusafos, and other nematicides.

When the active pesticidal compounds of the present invention are used in combination with one or more of second compounds, e.g., with other materials such as plant growth regulators, the plant growth regulators include, for example: maleic hydrazide, chlormequat, ethephon, gibberellin, mepiquat, thidiazon, inabenfide, triaphenthenol, paclobutrazol, unaconazol, DCPA, prohexadione, trinexapac-ethyl, and other plant growth regulators.

Soil conditioners are materials which, when added to the soil, promote a variety of benefits for the efficacious growth of plants. Soil conditioners are used to

reduce soil compaction, promote and increase effectiveness of drainage, improve soil permeability, promote optimum plant nutrient content in the soil, and promote better pesticide and fertilizer incorporation. When the active pesticidal compounds of the present invention are used in combination with one or more of second compounds, e.g., with other materials such as soil conditioners, the soil conditioners include organic matter, such as humus, which promotes retention of cation plant nutrients in the soil; mixtures of cation nutrients, such as calcium, magnesium, potash, sodium, and hydrogen complexes; or microorganism compositions which promote conditions in the soil favorable to plant growth. Such microorganism compositions include, for example, *bacillus, pseudomonas, azotobacter, azospirillum, rhizobium*, and soil-borne *cyanobacteria.*

Fertilizers are plant food supplements, which commonly contain nitrogen, phosphorus, and potassium. When the active pesticidal compounds of the present invention are used in combination with one or more of second compounds, e.g., with other materials such as fertilizers, the fertilizers include nitrogen fertilizers, such as ammonium sulfate, ammonium nitrate, and bone meal; phosphate fertilizers, such as superphosphate, triple superphosphate, ammonium sulfate, and diammonium sulfate; and potassium fertilizers, such as muriate of potash, potassium sulfate, and potassium nitrate, and other fertilizers.

In some cases, the effectiveness of such combinations may be improvement. For example, such combinations may exhibit synergistic effects, reduced rates of application resulting in improved user safety, control a broader spectrum of pests, improved tolerance by plants, and improved tolerance by non-pest species, such as mammals and fish.

The methods of the present invention are predicated on causing an insecticidal or acaricidal amount of a compound of Formula I to be present within insects or acarids and, thereby, killing or controlling the insects or acarids. It is possible and is within the scope of the invention to cause a compound of Formula I wherein R^5, R^6 and R^7 represent amino (NH_2) to be present within insects or acarids by contacting the insects or acarids with a derivative of that compound, which derivative is converted within the insects or acarids to a compound of Formula I wherein R^5, R^6 and R^7 represent amino. Such compounds, which can be referred to

as pro-insecticides, include compounds containing an R^5, R^6 and R^7 substituent that can be converted to NH_2 by chemical processes, such as hydrolysis, oxidation, reduction, and the like, that are either enzymatic or non-enzymatic in nature. Suitable substituents include N-acylamino, N-substituted imino, and N-sulfenyl amino groups, and the like. Some examples, wherein hydrocarbyl refers to an aliphatic or aromatic hydrocarbon moiety optionally substituted with halogen, hydroxy, alkoxy, cyano, or nitro, or the like, are illustrated below:

NH-CO(hydrocarbyl); NH-CH(OH)(hydrocarbyl); NH-CO_2(hydrocarbyl); N=CH(hydrocarbyl); NH-CO-NH(hydrocarbyl); NH-S(hydrocarbyl); NH-$COCO_2$(hydrocarbyl); NH-S-N(hydrocarbyl)$_2$; NH-C(S-(hydrocarbyl))=N(hydrocarbyl); NH-CH(O-(hydrocarbyl))(hydrocarbyl)

Compounds containing such substituents can be prepared from compounds of Formula I wherein R^5, R^6 and R^7 represent NH_2 by well established methods known to those in the art. For example, N-acyl derivatives can be prepared by treatment with an acyl halide or anhydride, N-substituted imino derivatives can be prepared by treatment with aldehydes, urea derivatives can be prepared by treatment with isocyanates, N-sulfenyl derivatives can be prepared by treatment with a sulfenyl chloride, carbamate derivatives can be prepared by treatment with a chloroformate ester, and isothiourea derivatives can be prepared by treatment with first an isothiocyanate and then a hydrocarbyl halide.

It is further possible and within the scope of the invention to cause a compound of Formula I wherein R^5, R^6 and R^7 represent hydroxy (OH) to be present within insects or acarids by contacting the insects or acarids with a derivative of that compound, which derivative is converted within the insects or acarids to a compound of Formula I wherein R^5, R^6 and R^7 represent hydroxy. Such compounds are also pro-insecticides. Suitable compounds include compounds containing an R^5, R^6 and R^7 substituent that can be converted to OH by chemical processes, such as hydrolysis, oxidation, reduction, and the like, that are either enzymatic or non-enzymatic in nature. Typical substituents include acyloxy, carbamoyloxy, and carbonyl. Some examples, wherein hydrocarbyl refers to an aliphatic or aromatic

hydrocarbon moiety optionally substituted with halogen, hydroxy, alkoxy, cyano, or nitro, or the like are illustrated below:

O-CO(hydrocarbyl; O-CH_3; O-CO_2(hydrocarbyl); O-$C(CH_3)_2$-O-hyrdocarboyl; O-C(O)-N(hydrocarbyl)$_2$; O-CH_2OCH_3; O-C(O)-NH_2; O-$CH_2CH{=}CH_2$; O-$SO_3^-M^+$; O-$PO_3^-M^+$

Compounds of these types can be prepared from compounds of Formula I wherein R^5, R^6 and R^7 represent OH by methods well established in the art. For example, acyloxy derivatives may be prepared by treatment with acid halides or anhydrides; carbamoyloxy derivatives can be prepared by treatment with a carbamoyl chloride; and carbonyl derivatives can be prepared by treatment with a carbonate or chloroformate.

It is further possible and within the scope of the invention to cause a compound of Formula I wherein R^5, R^6 and R^7 represent mercapto or thiol (SH) to be present within insects or acarids by contacting the insects or acarids with a derivative of that compound, which derivative is converted within the insects or acarids to a compound of Formula I wherein R^5, R^6 and R^7 represent mercapto. Such compounds are also pro-insecticides. Suitable compounds include compounds containing an R^5, R^6 and R^7 substituent that can be converted to SH by chemical processes, such as hydrolysis, oxidation, reduction, and the like, that are either enzymatic or non-enzymatic in nature. Typical substituents include acylthio and hydrocarbyloxyalkylthio, wherein hydrocarbyl refers to an aliphatic or aromatic hydrocarbon moiety optionally substituted with halogen, hydroxy, alkoxy, cyano, or nitro, or the like. Some examples are illustrated below:

S-C(O)-hydrocarbyl; S-CH_2O_2C(hydrocarbyl); S-CH_3; S-C(O)-aryl

Compounds of these types can be prepared from a compound of Formula I wherein R^5, R^6 and R^7 represent SH by methods well established in the art. For example, acylthio derivatives may be prepared by treatment with acyl halides or anhydrides and hydrocarbyloxyalkylthio derivatives may be prepared by treatment with a hydrocarbylheteroalkyl halide.

The present invention also includes the use of the compounds and compositions set forth herein for control of non-agricultural insect species, for

example, dry wood termites and subterranean termites; as well as for use as pharmaceutical agents. In the field of veterinary medicine, the compounds of the present invention are expected to be effective against certain *endo-* and *ecto-* parasites, such as insects and worms, which prey on animals. Examples of such animal parasites include, without limitation, *Gastrophilus* spp., *Stomoxys* spp., *Trichodectes* spp., *Rhodnius* spp., Ctenocephalides canis, and other species.

The following examples further illustrate the present invention, but, of course, should not be construed as in any way limiting its scope. The examples are organized to present protocols for the synthesis of the compounds of formula **I** of the present invention, set forth a list of such synthesized species, and set forth certain biological data indicating the efficacy of such compounds.

EXAMPLE 1

This example illustrates one protocol for the preparation of the N-oxide of 2-(4-azabicyclo[2.2.1]heptyl-2-yl)-5-methyl-1,2,3,4-tetrazole (Compound 402).

The intermediate 2-(4-azabicyclo[2.2.1]heptyl-2-yl)-5-methyl-1,2,3,4-tetrazole (prepared by Jenkins et al as Compound 2o in *J. Med. Chem*, 1992, *35*, 2392-2406), 0.03 gram (0.00017 mole), was taken up in 1 mL of chloroform. Upon dissolution, the solution was cooled to 0°C and 0.041 gram (0.00018 mole) of *meta*-chloroperbenzoic acid was added in three portions. Upon completion of addition, the reaction mixture was allowed to warm to ambient temperature where it stirred for about 20 minutes. Upon completion of this period, the reaction mixture was analyzed by TLC, which indicated that the reaction was complete. The reaction mixture was subjected to small column chromatography on neutral alumina. The product-containing fractions were combined and concentrated under reduced pressure, yielding 0.029 gram of Compound 402. The NMR spectrum was consistent with the proposed structure.

EXAMPLE 2

This example illustrates one protocol for the preparation of the N-oxide of 3-[1-methyl(1,2,5,6-tetrahydropyrid-3-yl)]-1,2,5-thiadiazole (Compound 6).

The intermediate 3-[1-methyl(1,2,5,6-tetrahydropyrid-3-yl)]-1,2,5-thiadiazole (prepared by Sauerburg as compound 11 in *J. Med. Chem*, 1992, *35*, 2274-2283) was converted to the N-oxide (compound 6) in by the method set forth in Example 1; using 0.05 gram (0.000265 mole) of the intermediate 1,2,5-thiadiazole, and 0.07 gram (0.000270 mole) of *meta*-chloroperbenzoic acid in 10 mL of methylene chloride. The reaction mixture was subjected to small column chromatography on silica gel. The product-containing fractions were combined and concentrated under reduced pressure, yielding 0.045 gram of Compound 6. The NMR spectrum was consistent with the proposed structure.

EXAMPLE 3

This example illustrates one protocol for the preparation of the N-oxide of 5-(4-azabicyclo[2.2.1]hept-2-yl)-3-methyl-1,2,4-oxadiazole (Compound 396).

The intermediate 5-(4-azabicyclo[2.2.1]hept-2-yl)-3-methyl-1,2,4-oxadiazole (prepared by Orlek as compound 7b in *J. Med. Chem*, 1991, *34*, 2726-2735) was converted to the N-oxide (compound 396) by the method set forth in Example 1; using 0.28 gram (0.000156 mole) of the intermediate 1,2,4-oxadiazole, and 0.035 gram (0.000156 mole) of *meta*-chloroperbenzoic acid in 6 mL of a mixture of methylene chloride and chloroform. The reaction mixture was subjected to small column chromatography on silica gel. The product-containing fractions were combined and concentrated under reduced pressure, yielding 0.030 gram of Compound 396. The NMR spectrum was consistent with the proposed structure.

EXAMPLE 4

This example illustrates one protocol for the preparation of the N-oxide of 5-methyl-2-quinuclidin-3-yl-1,2,3,4-tetraazole (Compound 407).

The intermediate 5-methyl-2-quinuclidin-3-yl-1,2,3,4-tetraazole (prepared by Wadsworth et al as compound 28 in *J. Med. Chem*, 1992, *35*, 1280-1290) was converted to the N-oxide (compound 407) by the method set forth in Example 1; using 0.060 gram (0.00031 mole) of the intermediate 1,2,3,4-tetraazole and 0.077 gram (0.00034 mole) of *meta*-chloroperbenzoic acid in 1.5 mL of chloroform. The

reaction mixture was subjected to small column chromatography on neutral alumina activity III (6% water). The product-containing fractions were combined and concentrated under reduced pressure, yielding 0.055 gram of Compound 407. The NMR spectrum was consistent with the proposed structure.

EXAMPLE 5

This example illustrates one protocol for the preparation of the N-oxide of 5-(4-azabicyclo[2.2.1]hept-2-yl)-3-ethyl-1,2,4-oxadiazole (Compound 397)

The intermediate 5-(4-azabicyclo[2.2.1]hept-2-yl)-3-ethyl-1,2,4-oxadiazole (prepared by Orlek as the ethyl derivative of compound 7b in *J. Med. Chem*, 1991, *34*, 2726-2735) was converted to the N-oxide (compound 397) by the method set forth in Example 1; using 0.05 gram (0.00026 mole) of the intermediate 1,2,4-oxadiazole, and 0.064 gram (0.00029 mole) of *meta*-chloroperbenzoic acid in 2 mL of chloroform. The reaction mixture was subjected to small column chromatography on silica gel. The product-containing fractions were combined and concentrated under reduced pressure, yielding 0.025 gram of Compound 397. The NMR spectrum was consistent with the proposed structure.

EXAMPLE 6

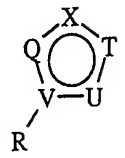
This example illustrates one protocol for the preparation of the N-oxide of 2-(5-azabicyclo[3.2.1]octyl)-5-methyl-1,3,4-oxadiazole (Compound 685).

The intermediate 2-(5-azabicyclo[3.2.1]octyl)-5-methyl-1,3,4-oxadiazole (prepared by Orlek as compound 9b in *J. Med. Chem*, 1991, *34*, 2726-2735) was converted to the N-oxide (compound 685) by thr method set forth in Example 1; using 0.060 gram (0.00031 mole) of the intermediate 1,3,4-oxadiazole and 0.084 gram (0.00037 mole) of *meta*-chloroperbenzoic acid in about 2 mL of chloroform. The reaction mixture was subjected to small column chromatography on neutral alumina. The product-containing fractions were combined and concentrated under reduced pressure, yielding about 0.040 gram of Compound 685. The NMR spectrum was consistent with the proposed structure.

The following table sets forth some compounds of formula I:

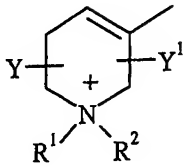
Table 1

Pesticidal N-Substituted Azacyclic Derivatives



I

where R is an azacycle selected from:



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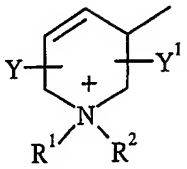

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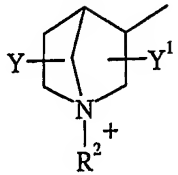

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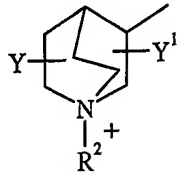

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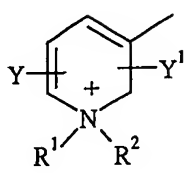

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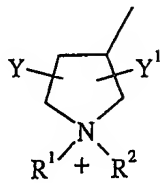

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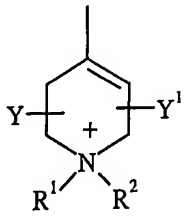

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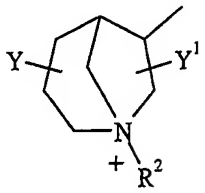

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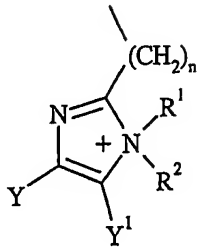

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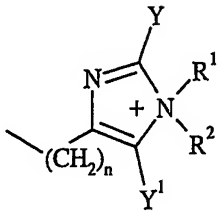

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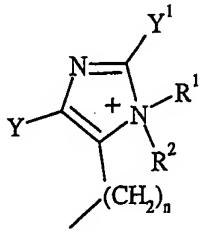

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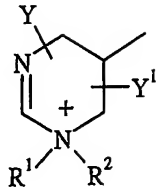

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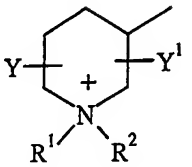

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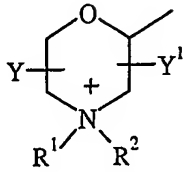

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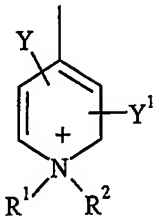
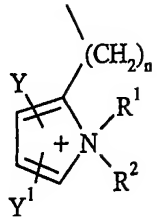


W15



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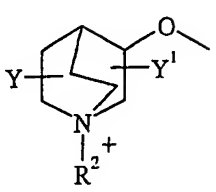

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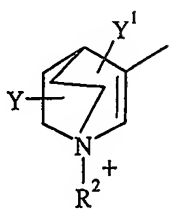

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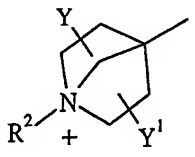

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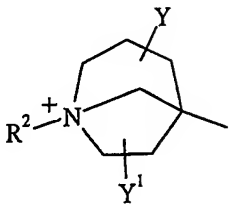

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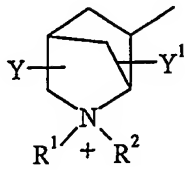

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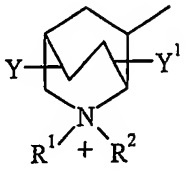

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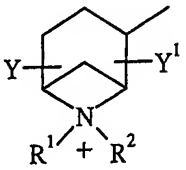

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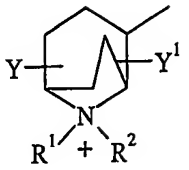

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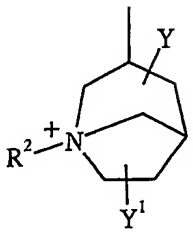

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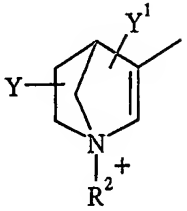

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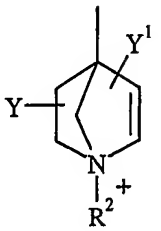

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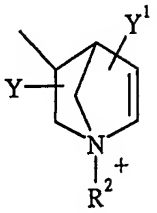

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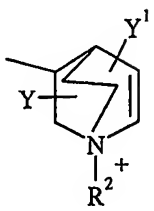

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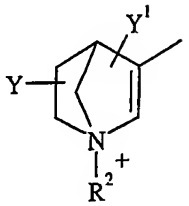

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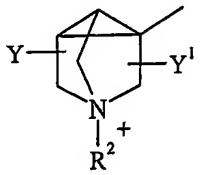

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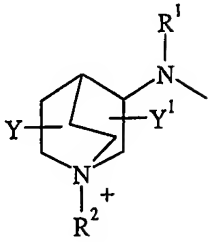

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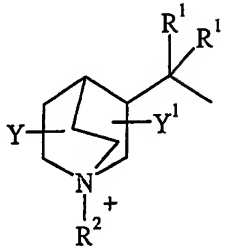

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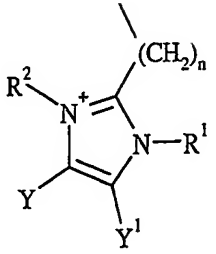

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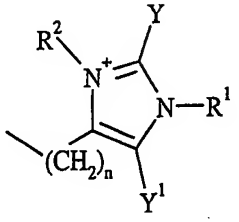

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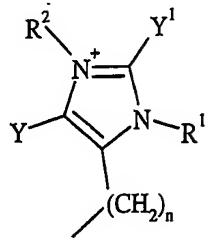

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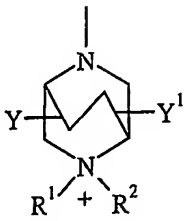

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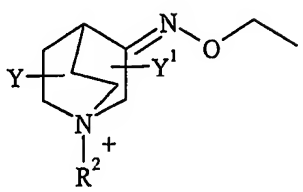

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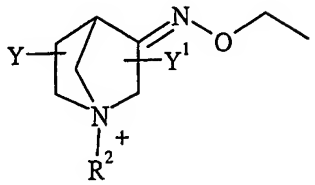

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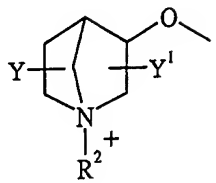
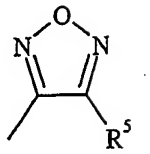


W40

and

is a five-membered heterocycle selected from:



X1
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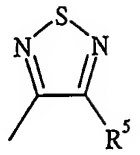

X2
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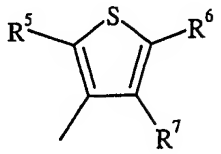
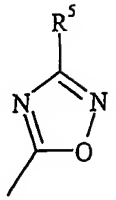
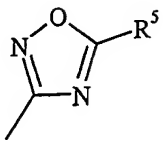


X3
a thien-3-yl



X4
a 1,2,4-oxadiazol-5-yl



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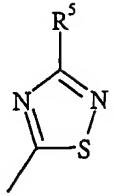

X6
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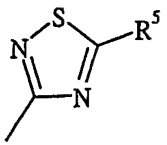

X7
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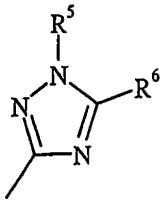

X8
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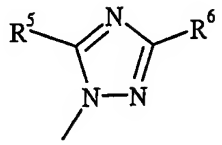

X9
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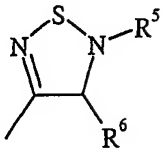

X10
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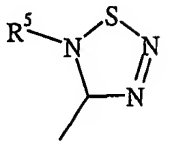

X11
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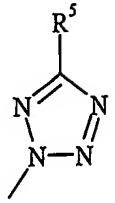

X12
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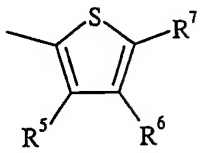
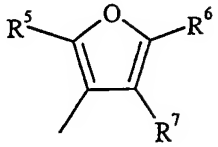
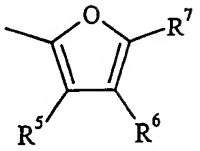


X13
a thien-2-yl



X14
a furan-3-yl



X15
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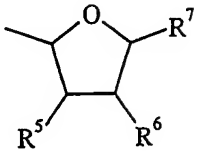
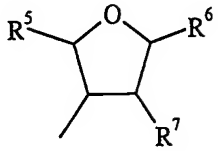


X16
a tetrahydrofuran-2-yl



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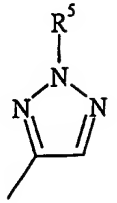

X18
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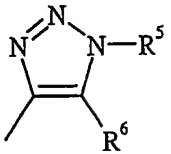

X19
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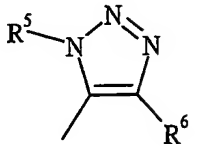

X20
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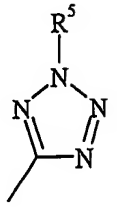
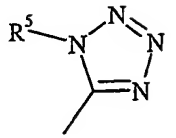


X21
a tetraazol-5-yl



X22
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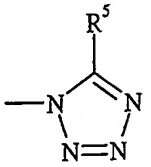

X23
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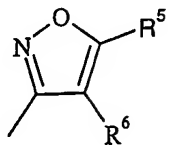

X24
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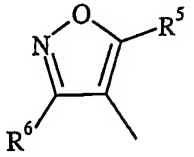

X25
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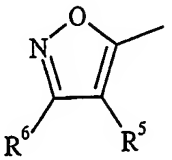

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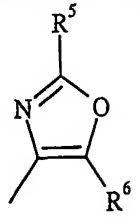

X27
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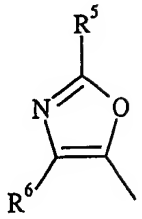

X28
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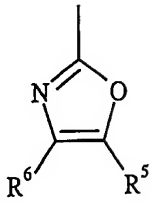

X29
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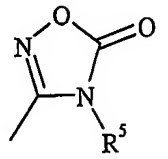
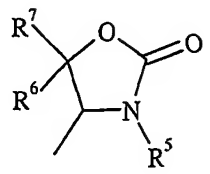
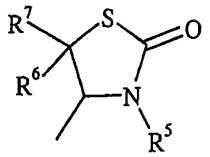


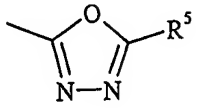
X30
a 2-oxadiazolidinon-4-yl



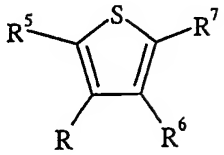
X31
a 2-oxazolidinon-4-yl



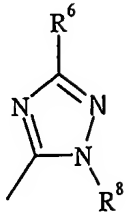
X32
a 2-thazolidinon-4-yl



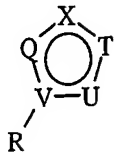
X33
a 1,3,4-oxadiazol-2-yl



X34
a thien-3-yl

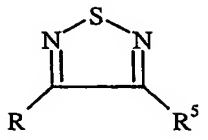


X35
a 1H-1,2,4-triazol-5-yl



I

where the five-membered heterocycle is X2, a 1,2,5-thiadiazol-3-yl



I

Cmpd. No.	R	R^5	R^1	R^2	Y	Y^1	n
1	W1	H	$-CH_2Ph$	O^-	H	H	---
2	W1	Cl	H	O^-	H	H	---
3	W1	Cl	$-CH_2Ph$	O^-	H	H	---
4	W1	F	$-CH_2Ph$	O^-	H	H	---
5	W1	Cl	$-CO_2C_2H_5$	O^-	H	H	---
6	W1	H	$-CH_3$	O^-	H	H	---
7	W1	H	$-CH_3$	O^-	2-Cl	H	---
8	W1	H	$-CH_3$	O^-	$2-CH_3$	H	---
9	W1	H	$-CH_3$	O^-	4-Cl	H	---
10	W1	H	$-CH_3$	O^-	$4-CH_3$	H	---
11	W1	H	$-CH_3$	O^-	6-Cl	H	---
12	W1	H	$-CH_3$	O^-	$6-CH_3$	H	---
13	W1	H	$-CH_3$	O^-	2-F	2-F	---
14	W1	H	$-CH_3$	O^-	$2-CH_3$	$2-CH_3$	---
15	W1	H	$-CH_3$	O^-	6-F	6-F	---
16	W1	H	$-CH_3$	O^-	$6-CH_3$	$6-CH_3$	---
17	W1	H	$-C_2H_5$	O^-	H	H	---
18	W1	H	$-CH_2OCH_3$	O^-	H	H	---
19	W1	Cl	$-CH_3$	O^-	H	H	---
20	W1	F	$-CH_3$	O^-	H	H	---
21	W1	F	$-CH_3$	O^-	2-Cl	H	---
22	W1	F	$-CH_3$	O^-	2-F	H	---
23	W1	F	$-CH_3$	O^-	$2-CH_3$	H	---
24	W1	F	$-CH_3$	O^-	4-Cl	H	---
25	W1	F	$-CH_3$	O^-	4-F	H	---
26	W1	F	$-CH_3$	O^-	$4-CH_3$	H	---
27	W1	F	$-CH_3$	O^-	6-Cl	H	---
28	W1	F	$-CH_3$	O^-	6-F	H	---
29	W1	F	$-CH_3$	O^-	$6-CH_3$	H	---
30	W1	F	$-CH_3$	O^-	2-Cl	2-Cl	---
31	W1	F	$-CH_3$	O^-	2-F	2-F	---
32	W1	F	$-CH_3$	O^-	$2-CH_3$	$2-CH_3$	---
33	W1	F	$-CH_3$	O^-	6-Cl	6-Cl	---
34	W1	F	$-CH_3$	O^-	6-F	6-F	---
35	W1	F	$-CH_3$	O^-	$6-CH_3$	$6-CH_3$	---
36	W1	$-CH_3$	$-CH_3$	O^-	H	H	---
37	W1	$-CH_3$	$-CH_3$	O^-	2-Cl	H	---
38	W1	$-CH_3$	$-CH_3$	O^-	2-F	H	---
39	W1	$-CH_3$	$-CH_3$	O^-	$2-CH_3$	H	---
40	W1	$-CH_3$	$-CH_3$	O^-	4-Cl	H	---
41	W1	$-CH_3$	$-CH_3$	O^-	4-F	H	---

Cmpd. No.	R	R^5	R^1	R^2	Y	Y^1	n
42	W1	$-CH_3$	$-CH_3$	O^-	4-CH_3	H	---
43	W1	$-CH_3$	$-CH_3$	O^-	6-Cl	H	---
44	W1	$-CH_3$	$-CH_3$	O^-	6-F	H	---
45	W1	$-CH_3$	$-CH_3$	O^-	6-CH_3	H	---
46	W1	$-CH_3$	$-CH_3$	O^-	2-Cl	2-Cl	---
47	W1	$-CH_3$	$-CH_3$	O^-	2-F	2-F	---
48	W1	$-CH_3$	$-CH_3$	O^-	2-CH_3	2-CH_3	---
49	W1	$-CH_3$	$-CH_3$	O^-	6-Cl	6-Cl	---
50	W1	$-CH_3$	$-CH_3$	O^-	6-F	6-F	---
51	W1	$-CH_3$	$-CH_3$	O^-	6-CH_3	6-CH_3	---
52	W1	$-CH_2CH_2C_6H_5$	$-CH_3$	O^-	H	H	---
53	W1	$-OCH_3$	$-CH_3$	O^-	H	H	---
54	W1	$-OC_2H_5$	$-CH_3$	O^-	H	H	---
55	W1	$-OC_3H_7$	$-CH_3$	O^-	H	H	---
56	W1	4-FPhO-	$-CH_3$	O^-	H	H	---
57	W1	$-OCH_2CH=CH_2$	$-CH_3$	O^-	H	H	---
58	W1	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	---
59	W1	$-OCH_2C\equiv CCH_3$	$-CH_3$	O^-	H	H	---
60	W1	$-SCH_3$	$-CH_3$	O^-	H	H	---
61	W1	$-SC_2H_5$	$-CH_3$	O^-	H	H	---
62	W1	$-SC_3H_7$	$-CH_3$	O^-	H	H	---
63	W1	$-SC_4H_9$	$-CH_3$	O^-	H	H	---
64	W1	$-SC_5H_{11}$	$-CH_3$	O^-	H	H	---
65	W1	$-SC_5H_{10}CN$	$-CH_3$	O^-	H	H	---
66	W1	$-SCH_2CH=CH_2$	$-CH_3$	O^-	H	H	---
67	W1	$-SCH_2C\equiv CH$	$-CH_3$	O^-	H	H	---
68	W2	$-CO_2C_4H_9$	$-CH_3$	O^-	H	H	---
69	W3	H	---	O^-	H	H	---
70	W3	H	---	O^-	2-F	H	---
71	W3	H	---	O^-	2-CH_3	H	---
71	W3	H	---	O^-	4-Cl	H	---
72	W3	H	---	O^-	4-CH_3	H	---
73	W3	H	---	O^-	6-Cl	H	---
74	W3	H	---	O^-	6-F	H	---
75	W3	H	---	O^-	6-CH_3	H	---
76	W3	H	---	O^-	2-Cl	2-Cl	---
77	W3	H	---	O^-	2-CH_3	2-CH_3	---
78	W3	H	---	O^-	6-Cl	6-Cl	---
79	W3	H	---	O^-	6-F	6-F	---
80	W3	Cl	---	O^-	H	H	---
81	W3	F	---	O^-	H	H	---
82	W3	CH_3	---	O^-	H	H	---
83	W3	$-OCH_2C\equiv CH$	---	O^-	H	H	---
84	W4	H	---	O^-	H	H	---
85	W4	F	---	O^-	H	H	---
86	W4	Cl	---	O^-	H	H	---
87	W4	Cl	---	O^-	3-Cl	H	---
88	W4	Cl	---	O^-	2-Cl	2-Cl	---
89	W4	Cl	---	O^-	6-CH_3	6-CH_3	---
90	W4	$-OCH_3$	---	O^-	H	H	---
91	W4	$-OC_2H_5$	---	O^-	H	H	---
92	W4	$-OC_3H_7$	---	O^-	H	H	---
93	W4	$-OC_4H_9$	---	O^-	H	H	---
94	W4	$-OCH_2CH=CH_2$	---	O^-	H	H	---

Cmpd. No.	R	R^5	R^1	R^2	Y	Y^1	n
95	W4	$-OCH_2C\equiv CH$	---	O^-	H	H	---
96	W4	$-OCH_2C\equiv CCH_3$	---	O^-	H	H	---
97	W4	$-OCH_2CH_2C\equiv CH$	---	O^-	H	H	---
98	W4	$-SCH_3$	---	O^-	H	H	---
99	W4	$-SC_2H_5$	---	O^-	H	H	---
100	W4	$-SC_3H_7$	---	O^-	H	H	---
101	W4	$-SC_4H_9$	---	O^-	H	H	---
102	W4	$-SC_6H_{13}$	---	O^-	H	H	---
103	W4	$-SC_6H_{12}CN$	---	O^-	H	H	---
104	W4	$-SCH_2CH=CH_2$	---	O^-	H	H	---
105	W4	$-SCH_2C\equiv CH$	---	O^-	H	H	---
106	W4	$-SCH_2C\equiv CCH_3$	---	O^-	H	H	---
107	W4	$-SCH_2CH_2C\equiv CH$	---	O^-	H	H	---
108	W5	H	H	O^-	H	H	---
109	W5	Cl	H	O^-	H	H	---
110	W5	F	H	O^-	H	H	---
111	W5	$-CH_3$	H	O^-	H	H	---
112	W5	$-C_2H_5$	H	O^-	H	H	---
113	W5	$-C_3H_7$	H	O^-	H	H	---
114	W5	$-C_4H_9$	H	O^-	H	H	---
115	W5	$-OCH_3$	H	O^-	H	H	---
116	W5	$-OC_2H_5$	H	O^-	H	H	---
117	W5	$-OC_3H_7$	$-CH_3$	O^-	H	H	---
118	W5	$-OC_4H_9$	H	O^-	H	H	---
119	W5	$-OC_5H_{11}$	H	O^-	H	H	---
120	W5	$-OCH_2CH=CH_2$	H	O^-	H	H	---
121	W5	$-OCH_2C\equiv CCH_3$	H	O^-	H	H	---
122	W5	$-OCH_2CH_2C\equiv CH$	H	O^-	H	H	---
123	W5	$-SCH_3$	H	O^-	H	H	---
124	W5	$-SC_2H_5$	H	O^-	H	H	---
125	W5	$-SC_3H_7$	H	O^-	H	H	---
126	W5	$-SC_4H_9$	H	O^-	H	H	---
127	W5	$-SC_5H_{11}$	H	O^-	H	H	---
128	W5	$-SC_5H_{10}CN$	H	O^-	H	H	---
129	W5	$-SC_6H_{13}$	H	O^-	H	H	---
130	W5	$-SC_6H_{12}CN$	H	O^-	H	H	---
131	W5	$-SCH_2CH=CH_2$	H	O^-	H	H	---
132	W5	$-SCH_2C\equiv CH$	H	O^-	H	H	---
133	W5	$-SCH_2C\equiv CCH_3$	H	O^-	H	H	---
134	W5	$-SCH_2CH_2C\equiv CH$	H	O^-	H	H	---
135	W5	Cl	$-C(O)OC_2H_5$	O^-	H	H	---
136	W5	Cl	$-CH_2Ph$	O^-	H	H	---
137	W6	H	H	O^-	H	H	---
138	W6	Cl	H	O^-	H	H	---
139	W6	F	H	O^-	H	H	---
140	W6	$-CH_3$	H	O^-	H	H	---
141	W6	$-OCH_2C\equiv CCH_3$	H	O^-	H	H	---
142	W6	H	$-CH_3$	O^-	H	H	---
143	W6	Cl	$-CH_3$	O^-	H	H	---
144	W6	F	$-CH_3$	O^-	H	H	---
145	W6	$-CH_3$	$-CH_3$	O^-	H	H	---
146	W6	$-OCH_2C\equiv CCH_3$	$-CH_3$	O^-	H	H	---
147	W7	H	H	O^-	H	H	---
148	W7	Cl	H	O^-	H	H	---

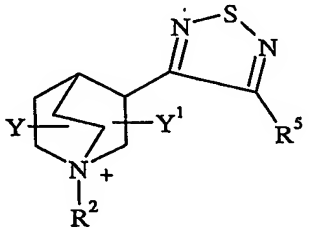
Cmpd. No.	R	R^5	R^1	R^2	Y	Y^1	n
149	W7	Cl	H	O^-	4-Cl	H	---
150	W7	F	H	O^-	H	H	---
151	W7	$-CH_3$	H	O^-	H	H	---
152	W7	$-OCH_2C\equiv CH$	H	O^-	H	H	---
153	W7	H	$-CH_3$	O^-	H	H	---
154	W7	Cl	$-CH_3$	O^-	H	H	---
155	W7	Cl	$-CH_3$	O^-	H	H	---
156	W7	F	$-CH_3$	O^-	H	H	---
157	W7	$-CH_3$	$-CH_3$	O^-	H	H	---
158	W7	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	---
159	W7	$-CH_3$	$-CH_3$	O^-	2-Cl	H	---
160	W7	$-CH_3$	$-CH_3$	O^-	2-F	H	---
161	W7	$-CH_3$	$-CH_3$	O^-	$2-CH_3$	H	---
162	W7	$-CH_3$	$-CH_3$	O^-	4-Cl	H	---
163	W7	$-CH_3$	$-CH_3$	O^-	4-F	H	---
164	W7	$-CH_3$	$-CH_3$	O^-	$4-CH_3$	H	---
165	W7	$-CH_3$	$-CH_3$	O^-	6-Cl	H	---
166	W7	$-CH_3$	$-CH_3$	O^-	6-F	H	---
167	W7	$-CH_3$	$-CH_3$	O^-	$6-CH_3$	H	---
168	W7	$-CH_3$	$-CH_3$	O^-	2-Cl	2-Cl	---
169	W7	$-CH_3$	$-CH_3$	O^-	2-F	2-F	---
170	W7	$-CH_3$	$-CH_3$	O^-	$2-CH_3$	$2-CH_3$	---
171	W7	$-CH_3$	$-CH_3$	O^-	6-Cl	6-Cl	---
172	W7	$-CH_3$	$-CH_3$	O^-	6-F	6-F	---
173	W7	$-CH_3$	$-CH_3$	O^-	$6-CH_3$	$6-CH_3$	---
174	W8	H	---	O^-	H	H	---
175	W8	H	---	O^-	H	H	---
176	W8	Cl	---	O^-	H	H	---
177	W8	F	---	O^-	H	H	---
178	W8	$-CH_3$	---	O^-	H	H	---
179	W8	$-OCH_2C\equiv CH$	---	O^-	H	H	---
180	W9	H	H	O^-	H	H	0
181	W9	Cl	H	O^-	H	H	0
182	W9	F	H	O^-	H	H	0
183	W9	$-CH_3$	H	O^-	H	H	0
184	W9	$-C_2H_5$	H	O^-	H	H	0
185	W9	$-OCH_3$	H	O^-	H	H	0
186	W9	$-CH_2OCH$	H	O^-	H	H	0
187	W9	$-OCH_2C\equiv CH$	H	O^-	H	H	0
188	W9	H	H	O^-	H	H	1
189	W9	Cl	H	O^-	H	H	1
190	W9	F	H	O^-	H	H	1
191	W9	$-CH_3$	H	O^-	H	H	1
192	W9	$-C_2H_5$	H	O^-	H	H	1
193	W9	$-OCH_3$	H	O^-	H	H	1
194	W9	$-CH_2OCH$	H	O^-	H	H	1
195	W9	$-OCH_2C\equiv CH$	H	O^-	H	H	1
196	W9	H	$-CH_3$	O^-	H	H	0
197	W9	Cl	$-CH_3$	O^-	H	H	0
198	W9	F	$-CH_3$	O^-	H	H	0
199	W9	$-CH_3$	$-CH_3$	O^-	H	H	0
200	W9	$-C_2H_5$	$-CH_3$	O^-	H	H	0
201	W9	$-OCH_3$	$-CH_3$	O^-	H	H	0
202	W9	$-CH_2OCH$	$-CH_3$	O^-	H	H	0

Cmpd. No.	R	R^5	R^1	R^2	Y	Y^1	n
203	W9	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	0
204	W9	H	$-CH_3$	O^-	H	H	1
205	W9	Cl	$-CH_3$	O^-	H	H	1
206	W9	F	$-CH_3$	O^-	H	H	1
207	W9	$-CH_3$	$-CH_3$	O^-	H	H	1
208	W9	$-C_2H_5$	$-CH_3$	O^-	H	H	1
209	W9	$-OCH_3$	$-CH_3$	O^-	H	H	1
210	W9	$-CH_2OCH$	$-CH_3$	O^-	H	H	1
211	W9	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	1
212	W9	H	$-CH_3$	O^-	H	H	2
213	W9	Cl	$-CH_3$	O^-	H	H	2
214	W9	F	$-CH_3$	O^-	H	H	2
215	W9	$-CH_3$	$-CH_3$	O^-	H	H	2
216	W9	$-C_2H_5$	$-CH_3$	O^-	H	H	2
217	W9	$-OCH_3$	$-CH_3$	O^-	H	H	2
218	W9	$-CH_2OCH$	$-CH_3$	O^-	H	H	2
219	W9	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	2
220	W10	H	$-CH_3$	O^-	H	H	0
221	W10	Cl	$-CH_3$	O^-	H	H	0
222	W10	F	$-CH_3$	O^-	H	H	0
223	W10	$-CH_3$	$-CH_3$	O^-	H	H	0
224	W10	$-C_2H_5$	$-CH_3$	O^-	H	H	0
225	W10	$-OCH_3$	$-CH_3$	O^-	H	H	0
226	W10	$-CH_2OCH$	$-CH_3$	O^-	H	H	0
227	W10	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	0
228	W10	H	$-CH_3$	O^-	H	H	1
229	W10	Cl	$-CH_3$	O^-	H	H	1
230	W10	F	$-CH_3$	O^-	H	H	1
231	W10	$-CH_3$	$-CH_3$	O^-	H	H	1
232	W10	$-C_2H_5$	$-CH_3$	O^-	H	H	1
233	W10	$-OCH_3$	$-CH_3$	O^-	H	H	1
234	W10	$-CH_2OCH$	$-CH_3$	O^-	H	H	1
235	W10	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	1
236	W10	H	$-CH_3$	O^-	H	H	2
237	W10	Cl	$-CH_3$	O^-	H	H	2
238	W10	F	$-CH_3$	O^-	H	H	2
239	W10	$-CH_3$	$-CH_3$	O^-	H	H	2
240	W10	$-C_2H_5$	$-CH_3$	O^-	H	H	2
241	W10	$-OCH_3$	$-CH_3$	O^-	H	H	2
242	W10	$-CH_2OCH$	$-CH_3$	O^-	H	H	2
243	W10	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	2
244	W11	H	$-CH_3$	O^-	H	H	0
245	W11	Cl	$-CH_3$	O^-	H	H	0
246	W11	F	$-CH_3$	O^-	H	H	0
247	W11	$-CH_3$	$-CH_3$	O^-	H	H	0
248	W11	$-C_2H_5$	$-CH_3$	O^-	H	H	0
249	W11	$-OCH_3$	$-CH_3$	O^-	H	H	0
250	W11	$-CH_2OCH$	$-CH_3$	O^-	H	H	0
251	W11	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	0
252	W11	H	$-CH_3$	O^-	H	H	1
253	W11	Cl	$-CH_3$	O^-	H	H	1
254	W11	F	$-CH_3$	O^-	H	H	1
255	W11	$-CH_3$	$-CH_3$	O^-	H	H	1
256	W11	$-C_2H_5$	$-CH_3$	O^-	H	H	1

Cmpd. No.	R	R^5	$-R^1$	R^2	Y	Y^1	n
257	W11	$-OCH_3$	$-CH_3$	O^-	H	H	1
258	W11	$-CH_2OCH$	$-CH_3$	O^-	H	H	1
259	W11	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	1
260	W11	H	$-CH_3$	O^-	H	H	2
261	W11	Cl	$-CH_3$	O^-	H	H	2
262	W11	F	$-CH_3$	O^-	H	H	2
263	W11	$-CH_3$	$-CH_3$	O^-	H	H	2
264	W11	$-C_2H_5$	$-CH_3$	O^-	H	H	2
265	W11	$-OCH_3$	$-CH_3$	O^-	H	H	2
266	W11	$-CH_2OCH$	$-CH_3$	O^-	H	H	2
267	W11	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	2
268	W12	H	H	O^-	H	H	---
269	W12	H	$-CH_3$	O^-	H	H	---
270	W12	H	$-C_2H_5$	O^-	H	H	---
271	W12	H	$-OCH_3$	O^-	H	H	---
272	W12	H	$-CH_2OCH$	O^-	H	H	---
273	W12	H	$-OCH_2C\equiv CH$	O^-	H	H	---
274	W12	H	$-CO_2C_4H_9$	O^-	H	H	---
275	W12	Cl	H	O^-	H	H	---
276	W12	Cl	$-CH_3$	O^-	H	H	---
277	W12	Cl	$-C_2H_5$	O^-	H	H	---
278	W12	Cl	$-OCH_3$	O^-	H	H	---
279	W12	Cl	$-CH_2OCH$	O^-	H	H	---
280	W12	Cl	$-OCH_2C\equiv CH$	O^-	H	H	---
281	W12	Cl	$-CO_2C_4H_9$	O^-	H	H	---
282	W12	F	H	O^-	H	H	---
283	W12	F	$-CH_3$	O^-	H	H	---
284	W12	F	$-C_2H_5$	O^-	H	H	---
285	W12	F	$-OCH_3$	O^-	H	H	---
286	W12	F	$-CH_2OCH$	O^-	H	H	---
287	W12	F	$-OCH_2C\equiv CH$	O^-	H	H	---
288	W12	F	$-CO_2C_4H_9$	O^-	H	H	---
289	W12	$-CH_3$	H	O^-	H	H	---
290	W12	$-CH_3$	$-CH_3$	O^-	H	H	---
291	W12	$-CH_3$	$-C_2H_5$	O^-	H	H	---
292	W12	$-CH_3$	$-OCH_3$	O^-	H	H	---
293	W12	$-CH_3$	$-CH_2OCH$	O^-	H	H	---
294	W12	$-CH_3$	$-OCH_2C\equiv CH$	O^-	H	H	---
295	W12	$-CH_3$	$-CO_2C_4H_9$	O^-	H	H	---
296	W12	$-OCH_3$	H	O^-	H	H	---
297	W12	$-OCH_3$	$-CH_3$	O^-	H	H	---
298	W12	$-OCH_3$	$-C_2H_5$	O^-	H	H	---
299	W12	$-OCH_3$	$-OCH_3$	O^-	H	H	---
300	W12	$-OCH_3$	$-CH_2OCH$	O^-	H	H	---
301	W12	$-OCH_3$	$-OCH_2C\equiv CH$	O^-	H	H	---
302	W12	$-OCH_3$	$-CO_2C_4H_9$	O^-	H	H	---
303	W12	$-CH_2OCH$	H	O^-	H	H	---
304	W12	$-CH_2OCH$	$-CH_3$	O^-	H	H	---
305	W12	$-CH_2OCH$	$-C_2H_5$	O^-	H	H	---
306	W12	$-CH_2OCH$	$-OCH_3$	O^-	H	H	---
307	W12	$-CH_2OCH$	$-CH_2OCH$	O^-	H	H	---
308	W12	$-CH_2OCH$	$-OCH_2C\equiv CH$	O^-	H	H	---
309	W12	$-CH_2OCH$	$-CO_2C_4H_9$	O^-	H	H	---
310	W12	$-OCH_2C\equiv CH$	H	O^-	H	H	---

Cmpd. No.	R	R^5	R^1	R^2	Y	Y^1	n
311	W12	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	---
312	W12	$-OCH_2C\equiv CH$	$-C_2H_5$	O^-	H	H	---
313	W12	$-OCH_2C\equiv CH$	$-OCH_3$	O^-	H	H	---
314	W12	$-OCH_2C\equiv CH$	$-CH_2OCH$	O^-	H	H	---
314	W12	$-OCH_2C\equiv CH$	$-OCH_2C\equiv CH$	O^-	H	H	---
316	W12	$-OCH_2C\equiv CH$	$-CO_2C_4H_9$	O^-	H	H	---
317	W13	H	$-CH_2Ph$	O^-	H	H	---
318	W13	Cl	$-CH_2Ph$	O^-	H	H	---
319	W13	F	$-CH_2Ph$	O^-	H	H	---

where R is W4 and the five-membered heterocycle is X2, a 1,2,5-thiadiazol-3-yl



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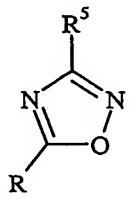
where R^5, Y and Y^1 are hydrogen

Cmpd No.	R^2	R^3	R^4
320	$-CH_3$	----	----
321	$-C_2H_5$	----	----
322	$-C_3H_7$	----	----
323	$-C_4H_9$	----	----
324	$-C_5H_{11}$	----	----
325	$-C_6H_{13}$	----	----
326	$-CH_2C_6H_5$	----	----
327	$4\text{-}FPhCH_2-$	----	----
328	$4\text{-}ClPhCH_2-$	----	----
329	$4\text{-}CH_3PhCH_2-$	----	----
330	$4\text{-}CH_3OPhCH_2-$	----	----
331	$3\text{-}ClPhCH_2-$	----	----
332	$3\text{-}CH_3PhCH_2-$	----	----
333	$3\text{-}(C_2H_5)PhCH_2-$	----	----
334	$2\text{-}ClPhCH_2-$	----	----
335	$-OCH_3$	----	----
336	$-OC_2H_5$	----	----
337	$-OC_3H_7$	----	----
338	$-OC_4H_9$	----	----
339	$-OC_5H_{11}$	----	----
340	$-OC_6H_{13}$	----	----
341	$-OCH_2Ph$	----	----

Cmpd No.	R^2	R^3	R^4
342	$-CH_2CO_2CH_3$	----	----
343	$-CH_2C(O)O^-$	----	----
344	$-C_2H_4CO_2CH_3$	----	----
345	$-C_2H_4C(O)O^-$	----	----
346	$-OC_2H_4SCH_3$	----	----
347	$-OC_2H_4S(O)CH_3$	----	----
348	$-OC_2H_4SO_2CH_3$	----	----
349	$-OC_2H_4PO_2OCH_3$	----	----
350	$-OC_2H_4PO_2O^-$	----	----
351	$-OC(O)CH_3$	----	----
352	$-OC(O)C_2H_5$	----	----
353	$-OC(O)C_3H_7$	----	----
354	$-OC(O)C_4H_9$	----	----
355	$-OC(O)C_5H_{11}$	----	----
356	$-OC(O)C_6H_{13}$	----	----
357	-OC(O)Ph	----	----
358	$-OC(O)CH_2Ph$	----	----
359	$-OCO_2CH_3$	----	----
360	$-OCO_2C_2H_5$	----	----
361	$-OCO_2C_3H_7$	----	----
362	$-OCO_2C_4H_9$	----	----
363	$-OCO_2C_5H_{11}$	----	----
364	$-OCO_2C_6H_{13}$	----	----
365	$-OCO_2Ph$	----	----
366	$-OCO_2CH_2Ph$	----	----
367	$-OC(O)N(R^3)(R^4)$	H	H
368	$-OC(O)N(R^3)(R^4)$	H	CH_3
369	$-OC(O)N(R^3)(R^4)$	H	C_2H_5
370	$-OC(O)N(R^3)(R^4)$	H	C_3H_7
371	$-OC(O)N(R^3)(R^4)$	H	C_4H_9
372	$-OC(O)N(R^3)(R^4)$	H	C_5H_{11}
373	$-OC(O)N(R^3)(R^4)$	H	C_6H_{13}
374	$-OC(O)N(R^3)(R^4)$	H	Ph
375	$-OC(O)N(R^3)(R^4)$	H	CH_2Ph
376	$-OC(O)N(R^3)(R^4)$	CH_3	CH_3
377	$-OC(O)N(R^3)(R^4)$	C_2H_5	C_2H_5
378	$-OC(O)N(R^3)(R^4)$	C_3H_7	C_3H_7
379	$-OC(O)N(R^3)(R^4)$	C_4H_9	C_4H_9
380	$-OC(O)N(R^3)(R^4)$	C_5H_{11}	C_5H_{11}
381	$-OC(O)N(R^3)(R^4)$	C_6H_{13}	C_6H_{13}
382	$-OC(O)N(R^3)(R^4)$	Ph	Ph
383	$-OC(O)N(R^3)(R^4)$	CH_2Ph	CH_2Ph
384	$-OC(O)N(R^3)(R^4)$	OCH_3	OCH_3
385	$-OC(O)N(R^3)(R^4)$	OC_2H_5	OC_2H_5
386	$-OC(O)N(R^3)(R^4)$	OC_3H_7	OC_3H_7
387	$-OC(O)N(R^3)(R^4)$	OC_4H_9	OC_4H_9
388	$-OC(O)N(R^3)(R^4)$	OC_5H_{11}	OC_5H_{11}
389	$-OC(O)N(R^3)(R^4)$	OC_6H_{13}	OC_6H_{13}
390	$-OC(O)N(R^3)(R^4)$	Oph	OPh
391	$-OC(O)N(R^3)(R^4)$	OCH_2Ph	OCH_2Ph
392	$-OC(O)N(R^3)(R^4)$	CH_3	C_2H_5
393	$-OC(O)N(R^3)(R^4)$	C_2H_5	C_3H_7
394	$-OC(O)N(R^3)(R^4)$	OCH_3	CH_3

where the five-membered heterocycle is X4, a 1,2,4-oxadiazol-5-yl



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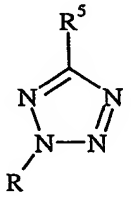
Cmpd. No.	R	R^1	R^2	R^5	Y	Y^1
395	W1	$-CH_3$	O^-	$-CH_3$	H	H
396	W3	---	O^-	$-CH_3$	H	H
397	W3	---	O^-	$-C_2H_5$	H	H
398	W3	---	O^-	$-OC_4H_9$	H	H
399	W4	---	O^-	$-CH_3$	H	H
400	W19	---	O^-	$-CH_3$	H	H
401	W20	---	O^-	$-CH_3$	H	H

where the five-membered heterocycle is X12, a 1,2,3,4-tetraazol-2-yl



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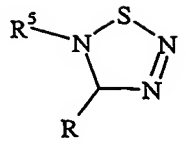
Cmpd No.	R	R^1	R^2	Y	Y^1	R^5
402[1]	W3	---	O^-	H	H	$-CH_3$
403[2]	W3	---	$-OCH_3$	H	H	$-CH_3$
404[3]	W3	---	O^-	H	H	$-CH_3$
405	W3	---	O^-	H	H	$-C_2H_5$
406	W3	---	O^-	H	H	$-NHC(=O)R^{9*}$
407	W4	---	O^-	H	H	$-CH_3$
408	W6	H	O^-	H	H	$-CH_3$

[1]Iodide salt; [2]*Exo*-isomer; [3]Bromide salt; *R^9 is $-CH_3$

where the five-membered heterocycle is X11, a 1,2,3,5-thiatriazolin-4-yl



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Cmpd No.	R	R^5	R^1	R^2	Y	Y^1	n
409	W1	H	H	O^-	H	H	---
410	W1	H	$-CH_2C_6H_5$	O^-	H	H	---
411	W1	H	$-C(O)OC_2H_5$	O^-	H	H	---
412	W1	H	$-CH_3$	O^-	H	H	---
413	W1	H	$-CH_3$	O^-	2-Cl	H	---
414	W1	H	$-CH_3$	O^-	$2-CH_3$	H	---
415	W1	H	$-CH_3$	O^-	4-Cl	H	---
416	W1	H	$-CH_3$	O^-	$4-CH_3$	H	---
417	W1	H	$-CH_3$	O^-	6-Cl	H	---
418	W1	H	$-CH_3$	O^-	$6-CH_3$	H	---
419	W1	H	$-CH_3$	O^-	2-F	2-F	---
420	W1	H	$-CH_3$	O^-	$2-CH_3$	$2-CH_3$	---
421	W1	H	$-CH_3$	O^-	6-F	6-F	---
422	W1	H	$-CH_3$	O^-	$6-CH_3$	$6-CH_3$	---
423	W1	H	$-C_2H_5$	O^-	H	H	---
424	W1	H	$-CH_2OCH_3$	O^-	H	H	---
425	W1	$-CH_3$	$-CH_3$	O^-	H	H	---
426	W1	$-CH_3$	$-CH_3$	O^-	2-Cl	H	---
427	W1	$-CH_3$	$-CH_3$	O^-	2-F	H	---
428	W1	$-CH_3$	$-CH_3$	O^-	$2-CH_3$	H	---
429	W1	$-CH_3$	$-CH_3$	O^-	4-Cl	H	---
430	W1	$-CH_3$	$-CH_3$	O^-	4-F	H	---
431	W1	$-CH_3$	$-CH_3$	O^-	$4-CH_3$	H	---
432	W1	$-CH_3$	$-CH_3$	O^-	6-Cl	H	---
433	W1	$-CH_3$	$-CH_3$	O^-	6-F	H	---
434	W1	$-CH_3$	$-CH_3$	O^-	$6-CH_3$	H	---
435	W1	$-CH_3$	$-CH_3$	O^-	2-Cl	2-Cl	---
436	W1	$-CH_3$	$-CH_3$	O^-	2-F	2-F	---
437	W1	$-CH_3$	$-CH_3$	O^-	$2-CH_3$	$2-CH_3$	---
438	W1	$-CH_2CH=CH_2$	$-CH_3$	O^-	6-Cl	6-Cl	---
439	W1	$-CH_2C\equiv CCH_3$	$-CH_3$	O^-	6-F	6-F	---
440	W1	$-OCH_2C\equiv CH$	$-CH_3$	O^-	$6-CH_3$	$6-CH_3$	---
441	W1	$-CH_2CH_2C_6H_5$	$-CH_3$	O^-	H	H	---
442	W1	$-OCH_3$	$-CH_3$	O^-	H	H	---
443	W1	$-OC_2H_5$	$-CH_3$	O^-	H	H	---
444	W1	$-OC_3H_7$	$-CH_3$	O^-	H	H	---
445	W1	4-FPhO	$-CH_3$	O^-	H	H	---
446	W1	$-OCH_2CH=CH_2$	$-CH_3$	O^-	H	H	---
447	W1	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	---
448	W1	$-OCH_2C\equiv CCH_3$	$-CH_3$	O^-	H	H	---
449	W1	$-SCH_3$	$-CH_3$	O^-	H	H	---
450	W1	$-SC_2H_5$	$-CH_3$	O^-	H	H	---
451	W1	$-SC_3H_7$	$-CH_3$	O^-	H	H	---
452	W1	$-SC_4H_9$	$-CH_3$	O^-	H	H	---
453	W1	$-SC_5H_{11}$	$-CH_3$	O^-	H	H	---

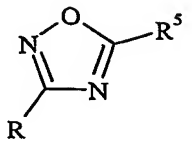
Cmpd No.	R	R^5	R^1	R^2	Y	Y^1	n
454	W1	$-SC_5H_{10}CN$	$-CH_3$	O^-	H	H	---
455	W1	$-SCH_2CH=CH_2$	$-CH_3$	O^-	H	H	---
456	W1	$-SCH_2C\equiv CH$	$-CH_3$	O^-	H	H	---
457	W1	$-CO_2C_4H_9$	$-CH_3$	O^-	H	H	---
458	W3	H	---	O^-	H	H	---
459	W3	H	---	O^-	2-F	H	---
460	W3	H	---	O^-	$2-CH_3$	H	---
461	W3	H	---	O^-	4-Cl	H	---
462	W3	H	---	O^-	$4-CH_3$	H	---
463	W3	H	---	O^-	6-Cl	H	---
464	W3	H	---	O^-	6-F	H	---
465	W3	H	---	O^-	$6-CH_3$	H	---
466	W3	H	---	O^-	2-Cl	2-Cl	---
467	W3	H	---	O^-	$2-CH_3$	$2-CH_3$	---
468	W3	H	---	O^-	6-Cl	6-Cl	---
469	W3	H	---	O^-	6-F	6-F	---
470	W3	$-CH_3$	---	O^-	H	H	---
471	W3	$-OCH_2C\equiv CH$	---	O^-	H	H	---
472	W4	H	---	O^-	H	H	---
473	W4	$-OCH_3$	---	O^-	H	H	---
474	W4	$-OC_2H_5$	---	O^-	H	H	---
475	W4	$-CH_2CH=CH_2$	---	O^-	H	H	---
476	W4	$-CH_2C\equiv CH$	---	O^-	H	H	---
377	W4	$-OCH_2CH=CH_2$	---	O^-	H	H	---
478	W4	$-OCH_2C\equiv CH$	---	O^-	H	H	---
479	W4	$-OCH_2C\equiv CCH_3$	---	O^-	H	H	---
480	W4	$-OCH_2CH_2C\equiv CH$	---	O^-	H	H	---
481	W4	$-SCH_3$	---	O^-	H	H	---
482	W4	$-SC_2H_5$	---	O^-	H	H	---
483	W4	$-SC_3H_7$	---	O^-	H	H	---
484	W4	$-SC_4H_9$	---	O^-	H	H	---
485	W4	$-SC_6H_{13}$	---	O^-	H	H	---
486	W4	$-SC_6H_{12}CN$	---	O^-	H	H	---
487	W4	$-SCH_2CH=CH_2$	---	O^-	H	H	---
488	W4	$-SCH_2C\equiv CH$	---	O^-	H	H	---
489	W4	$-SCH_2C\equiv CCH_3$	---	O^-	H	H	---
490	W4	$-SCH_2CH_2C\equiv CH$	---	O^-	H	H	---
491	W5	H	H	O^-	H	H	---
492	W5	$-CH_3$	H	O^-	H	H	---
493	W5	$-C_2H_5$	H	O^-	H	H	---
494	W5	$-C_3H_7$	H	O^-	H	H	---
495	W5	$-C_4H_9$	H	O^-	H	H	---
496	W5	$-OCH_3$	H	O^-	H	H	---
497	W5	$-OC_2H_5$	H	O^-	H	H	---
498	W5	$-OC_3H_7$	$-CH_3$	O^-	H	H	---
499	W5	$-OC_4H_9$	H	O^-	H	H	---
500	W5	$-OC_5H_{11}$	H	O^-	H	H	---
501	W5	$-OCH_2CH=CH_2$	H	O^-	H	H	---
502	W5	$-OCH_2C\equiv CCH_3$	H	O^-	H	H	---
503	W5	$-OCH_2CH_2C\equiv CH$	H	O^-	H	H	---
504	W5	$-SCH_3$	H	O^-	H	H	---
505	W5	$-SC_2H_5$	H	O^-	H	H	---
506	W5	$-SC_3H_7$	H	O^-	H	H	---
507	W5	$-SC_4H_9$	H	O^-	H	H	---

Cmpd No.	R	R^5	R^1	R^2	Y	Y^1	n
508	W5	$-SC_5H_{11}$	H	O^-	H	H	---
509	W5	$-SC_5H_{10}CN$	H	O^-	H	H	---
510	W5	$-SC_6H_{13}$	H	O^-	H	H	---
511	W5	$-SC_6H_{12}CN$	H	O^-	H	H	---
512	W5	$-SCH_2CH=CH_2$	H	O^-	H	H	---
513	W5	$-SCH_2C\equiv CH$	H	O^-	H	H	---
514	W5	$-SCH_2C\equiv CCH_3$	H	O^-	H	H	---
515	W5	$-SCH_2CH_2C\equiv CH$	H	O^-	H	H	---
516	W5	$-CH_2CH=CH_2$	$-CO_2C_2H_5$	O^-	H	H	---
517	W5	$-CH_2C\equiv CH$	$-CH_2Ph$	O^-	H	H	---
518	W6	H	H	O^-	H	H	---
519	W6	$-CH_3$	H	O^-	H	H	---
520	W6	$-OCH_2C\equiv CCH_3$	H	O^-	H	H	---
521	W6	H	$-CH_3$	O^-	H	H	---
522	W6	$-CH_3$	$-CH_3$	O^-	H	H	---
523	W6	$-OCH_2C\equiv CCH_3$	$-CH_3$	O^-	H	H	---
524	W7	H	H	O^-	H	H	---
525	W7	$-CH_3$	H	O^-	H	H	---
526	W7	$-OCH_2C\equiv CH$	H	O^-	H	H	---
527	W7	H	$-CH_3$	O^-	H	H	---
528	W7	$-CH_3$	$-CH_3$	O^-	H	H	---
529	W7	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	---
530	W7	$-CH_3$	$-CH_3$	O^-	2-Cl	H	---
531	W7	$-CH_3$	$-CH_3$	O^-	2-F	H	---
532	W7	$-CH_3$	$-CH_3$	O^-	$2-CH_3$	H	---
533	W7	$-CH_3$	$-CH_3$	O^-	4-Cl	H	---
534	W7	$-CH_3$	$-CH_3$	O^-	4-F	H	---
535	W7	$-CH_3$	$-CH_3$	O^-	$4-CH_3$	H	---
536	W7	$-CH_3$	$-CH_3$	O^-	6-Cl	H	---
537	W7	$-CH_3$	$-CH_3$	O^-	6-F	H	---
538	W7	$-CH_3$	$-CH_3$	O^-	$6-CH_3$	H	---
539	W7	$-CH_3$	$-CH_3$	O^-	2-Cl	2-Cl	---
540	W7	$-CH_3$	$-CH_3$	O^-	2-F	2-F	---
541	W7	$-CH_3$	$-CH_3$	O^-	$2-CH_3$	$2-CH_3$	---
542	W7	$-CH_3$	$-CH_3$	O^-	6-Cl	6-Cl	---
543	W7	$-CH_3$	$-CH_3$	O^-	6-F	6-F	---
544	W7	$-CH_3$	$-CH_3$	O^-	$6-CH_3$	$6-CH_3$	---
545	W8	H	---	O^-	H	H	---
546	W8	H	---	O^-	H	H	---
547	W8	$-CH_3$	---	O^-	H	H	---
548	W8	$-OCH_2C\equiv CH$	---	O^-	H	H	---
549	W9	H	H	O^-	H	H	0
550	W9	$-CH_3$	H	O^-	H	H	0
551	W9	$-C_2H_5$	H	O^-	H	H	0
552	W9	$-OCH_3$	H	O^-	H	H	0
553	W9	$-CH_2OCH$	H	O^-	H	H	0
554	W9	$-OCH_2C\equiv CH$	H	O^-	H	H	0
555	W9	H	H	O^-	H	H	1
556	W9	$-CH_3$	H	O^-	H	H	1
557	W9	$-C_2H_5$	H	O^-	H	H	1
558	W9	$-OCH_3$	H	O^-	H	H	1
559	W9	$-CH_2OCH$	H	O^-	H	H	1
560	W9	$-OCH_2C\equiv CH$	H	O^-	H	H	1
561	W9	H	$-CH_3$	O^-	H	H	0

Cmpd No.	R	R^5	R^1	R^2	Y	Y^1	n
562	W9	$-CH_3$	$-CH_3$	O^-	H	H	0
563	W9	$-C_2H_5$	$-CH_3$	O^-	H	H	0
564	W9	$-OCH_3$	$-CH_3$	O^-	H	H	0
565	W9	$-CH_2OCH$	$-CH_3$	O^-	H	H	0
566	W9	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	0
567	W9	H	$-CH_3$	O^-	H	H	1
568	W9	$-CH_3$	$-CH_3$	O^-	H	H	1
569	W9	$-C_2H_5$	$-CH_3$	O^-	H	H	1
570	W9	$-OCH_3$	$-CH_3$	O^-	H	H	1
571	W9	$-CH_2OCH$	$-CH_3$	O^-	H	H	1
572	W9	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	1
573	W9	H	$-CH_3$	O^-	H	H	2
574	W9	$-CH_3$	$-CH_3$	O^-	H	H	2
575	W9	$-C_2H_5$	$-CH_3$	O^-	H	H	2
576	W9	$-OCH_3$	$-CH_3$	O^-	H	H	2
577	W9	$-CH_2OCH$	$-CH_3$	O^-	H	H	2
578	W9	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	2
579	W10	H	$-CH_3$	O^-	H	H	0
580	W10	$-CH_3$	$-CH_3$	O^-	H	H	0
581	W10	$-C_2H_5$	$-CH_3$	O^-	H	H	0
582	W10	$-OCH_3$	$-CH_3$	O^-	H	H	0
583	W10	$-CH_2OCH$	$-CH_3$	O^-	H	H	0
584	W10	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	0
585	W10	$-CH_3$	$-CH_3$	O^-	H	H	1
586	W10	$-C_2H_5$	$-CH_3$	O^-	H	H	1
587	W10	$-OCH_3$	$-CH_3$	O^-	H	H	1
588	W10	$-CH_2OCH$	$-CH_3$	O^-	H	H	1
589	W10	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	1
590	W10	H	$-CH_3$	O^-	H	H	2
591	W10	$-CH_3$	$-CH_3$	O^-	H	H	2
592	W10	$-C_2H_5$	$-CH_3$	O^-	H	H	2
593	W10	$-OCH_3$	$-CH_3$	O^-	H	H	2
594	W10	$-CH_2OCH$	$-CH_3$	O^-	H	H	2
595	W10	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	2
596	W11	H	$-CH_3$	O^-	H	H	0
597	W11	$-CH_3$	$-CH_3$	O^-	H	H	0
598	W11	$-C_2H_5$	$-CH_3$	O^-	H	H	0
599	W11	$-OCH_3$	$-CH_3$	O^-	H	H	0
600	W11	$-CH_2OCH$	$-CH_3$	O^-	H	H	0
601	W11	$-CH_2C\equiv CH$	$-CH_3$	O^-	H	H	0
602	W11	H	$-CH_3$	O^-	H	H	1
603	W11	$-CH_3$	$-CH_3$	O^-	H	H	1
604	W11	$-C_2H_5$	$-CH_3$	O^-	H	H	1
605	W11	$-OCH_3$	$-CH_3$	O^-	H	H	1
606	W11	$-CH_2OCH$	$-CH_3$	O^-	H	H	1
607	W11	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	1
608	W11	H	$-CH_3$	O^-	H	H	2
609	W11	$-CH_3$	$-CH_3$	O^-	H	H	2
610	W11	$-C_2H_5$	$-CH_3$	O^-	H	H	2
611	W11	$-OCH_3$	$-CH_3$	O^-	H	H	2
612	W11	$-CH_2OCH$	$-CH_3$	O^-	H	H	2
613	W11	$-OCH_2C\equiv CH$	$-CH_3$	O^-	H	H	2
614	W12	H	H	O^-	H	H	---
615	W12	H	$-CH_3$	O^-	H	H	---

Cmpd No.	R	R^5	R^1	R^2	Y	Y^1	n
616	W12	H	$-C_2H_5$	O^-	H	H	---
617	W12	H	$-OCH_3$	O^-	H	H	---
618	W12	H	$-CH_2OCH$	O^-	H	H	---
619	W12	H	$-OCH_2C\equiv CH$	O^-	H	H	---
620	W12	H	$-CO_2C_4H_9$	O^-	H	H	---
621	W12	$-CH_3$	H	O^-	H	H	---
622	W12	$-CH_3$	$-CH_3$	O^-	H	H	---
623	W12	$-CH_3$	$-C_2H_5$	O^-	H	H	---
624	W12	$-CH_3$	$-OCH_3$	O^-	H	H	---
625	W12	$-CH_3$	$-CH_2OCH$	O^-	H	H	---
626	W12	$-CH_3$	$-OCH_2C\equiv CH$	O^-	H	H	---
627	W12	$-CH_3$	$-CO_2C_4H_9$	O^-	H	H	---
628	W12	$-OCH_3$	H	O^-	H	H	---
629	W12	$-OCH_3$	$-CH_3$	O^-	H	H	---
630	W12	$-OCH_3$	$-C_2H_5$	O^-	H	H	---
631	W12	$-OCH_3$	$-OCH_3$	O^-	H	H	---
632	W12	$-OCH_3$	$-CH_2OCH$	O^-	H	H	---
633	W12	$-OCH_3$	$-OCH_2C\equiv CH$	O^-	H	H	---
634	W12	$-OCH_3$	$-CO_2C_4H_9$	O^-	H	H	---
635	W12	$-CH_2OCH$	H	O^-	H	H	---
636	W12	$-CH_2OCH$	$-CH_3$	O^-	H	H	---
637	W12	$-CH_2OCH$	$-C_2H_5$	O^-	H	H	---
638	W12	$-CH_2OCH$	$-OCH_3$	O^-	H	H	---
639	W12	$-CH_2OCH$	$-CH_2OCH$	O^-	H	H	---
640	W12	$-CH_2OCH$	$-OCH_2C\equiv CH$	O^-	H	H	---
641	W12	$-CH_2OCH$	$-CO_2C_4H_9$	O^-	H	H	---
642	W12	$-CH_2CH=CH$	H	O^-	H	H	---
643	W12	$-CH_2CH=CH$	$-CH_3$	O^-	H	H	---
644	W12	$-OCH_2C\equiv CH$	$-C_2H_5$	O^-	H	H	---
645	W12	$-OCH_2C\equiv CH$	$-OCH_3$	O^-	H	H	---
646	W12	$-OCH_2C\equiv CH$	$-CH_2OCH$	O^-	H	H	---
647	W12	$-OCH_2C\equiv CH$	$-OCH_2C\equiv CH$	O^-	H	H	---
648	W12	$-OCH_2C\equiv CH$	$-CO_2C_4H_9$	O^-	H	H	---

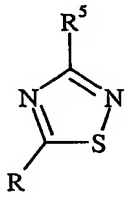
where the five-membered heterocycle is X5, a 1,2,4-oxadiazol-3-yl



I

Cmpd No.	R	R^1	R^2	R^5	Y	Y^1
649	W4	--	O^-	$-CH_3$	H	H

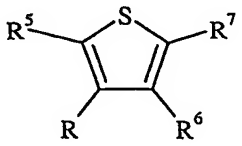
where the five-membered heterocycle is X6, a 1,2,4-thiadiazol-5-yl



I

Cmpd No.	R	R^1	R^2	R^5
650	W1	$-CH_3$	O^-	H
651	W1	$-CH_3$	O^-	$-CH_3$
652	W1	$-CH_2Ph$	O^-	$-CH_3$
653	W3	---	O^-	$-CH_3$
654	W3	---	O^-	H

where the five-membered heterocycle is X34, a thien-3-yl

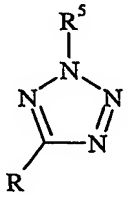


I

where R^6 and R^7 are hydrogen:

Cmpd No.	R	R^1	R^2	R^5
655	W1	$-CH_3$	O^-	H
656	W1	$-CH_3$	O^-	$-O(CH_2)_4CH_3$
657	W1	$-CH_3$	O^-	$-OCH_2C{\equiv}CCH_3$
658	W1	$-CH_2Ph$	O^-	$-O(CH_2)_4CH_3$
659	W3	---	O^-	H
660	W3	---	O^-	$-O(CH_2)_4CH_3$
661	W3	---	O^-	$-OCH_2C{\equiv}CCH_3$
662	W4	---	O^-	H
663	W4	---	O^-	$-O(CH_2)_4CH_3$
664	W4	---	O^-	$-OCH_2C{\equiv}CCH_3$

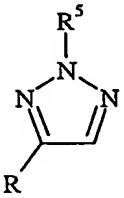
where the five-membered heterocycle is X21, a tetraazol-5-yl



I

Cmpd No.	R	R^1	R^2	R^5
665	W1	$-CH_3$	O^-	$-CH_3$
666	W1	$-CH_3$	O^-	$-C_2H_5$
667	W1	$-CH_3$	O^-	$-CH_2C{\equiv}CCH_3$
668	W1	$-CH_2Ph$	O^-	$-CH_3$
669	W3	---	O^-	$-CH_3$
670	W3	---	O^-	$-C_2H_5$
671	W3	---	O^-	$-CH_2C{\equiv}CCH_3$
672	W4	---	O^-	$-CH_3$
673	W4	---	O^-	$-C_2H_5$
674	W4	---	O^-	$-CH_2C{\equiv}CCH_3$

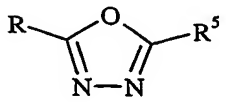
where the five-membered heterocycle is X18, a 1,2,3-triazol-4-yl



I

Cmpd No.	R	R^1	R^2	R^5
675	W1	$-CH_3$	O^-	$-CH_3$
676	W1	$-CH_3$	O^-	$-C_2H_5$
677	W1	$-CH_3$	O^-	$-CH_2C{\equiv}CCH_3$
678	W1	$-CH_3$	O^-	$-CH_2Ph$
679	W1	$-CH_2Ph$	O^-	$-CH_3$
680	W3	---	O^-	$-CH_3$
681	W3	---	O^-	$-C_2H_5$
682	W3	---	O^-	$-CH_2C{\equiv}CCH_3$
683	W3	---	O^-	$-CH_2Ph$

where the 5-membered heterocycle is X33, a 1,3,4-oxadiazol-2-yl



I

Cmpd No.	R	R^2	R^5
685	W20	O^-	$-CH_3$

Certain N-Substituted azacyclic compounds where the N-substituent is O^- (the N-oxides) of the present invention were tested to determine their translaminar characteristics as evidenced by activity against cotton aphid (*Aphis gossypii*) in comparison with their corresponding free amine derivatives. These tests were conducted in the following manner: For each compound tested, one cotton plant with two mature leaves was selected. On the top of one of the leaves a sticky material used for trapping insects was applied using a stamp of about 2.5 centimeters in diameter. The process was repeated on the bottom of the second leaf of the cotton plant. A solution of 500 ppm of test compound (dissolved in 1:1 acetone and water containing a small amount of surfactant) was then applied to the entire side of each leaf opposite the side stamped with the sticky material using a saturated cotton swab. Upon completion of the application of the test compounds, the cotton plants were maintained in a growth chamber for about 18 hours. After this time the leaves of the test plant were infested with a known number of cotton aphids by placing an infested leaf cutting from the cotton aphid colony directly over the sticky material on each

leaf. The leaf cutting on the bottom of a leaf of the test plant was secured to the leaf with a pin. The treated and infested cotton plants were then maintained in a chamber, during which time they were evaluated at daily intervals of from one to up to eight days. A test compound was termed active (A) if the top and bottom of the leaves of the test plant were mostly free of aphids (80% to 100%) when compared to untreated controls. A test compound was termed somewhat active (SA) if 50% to 80% of the aphids were eliminated, and inactive (I) if less than 50% of the aphids were eliminated. The results of these tests are set forth below:

Table 2

Comparison of Translaminar Insecticidal Activity of N-Oxides of Certain Azacyclic Derivatives and The Corresponding Free Amine Derivatives

Cmpd No.	Percent Mortality at Day After treatment (DAT)						
	1 DAT	2 DAT	3 DAT	4 DAT	5 DAT	6 DAT	7 DAT
6	--	SA	SA	--	SA	SA	--
A	I	I	I	I	--	I	--
396*	--	A	A	--	A	A	--
B	I	I	I	--	--	I	I
397	SA	--	SA	SA	SA	SA	--
C	I	--	I	I	I	I	--
402	A	A	A	--	--	A	A
D	--	--	--			SA	SA
407	I	--	SA	SA	SA	SA	--
E	I	--	I	I	I	I	--

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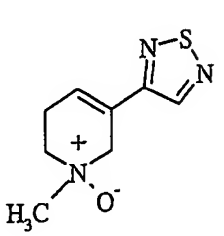
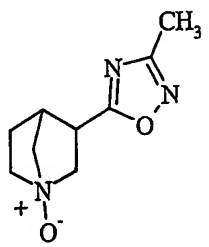
Rate of Application: 500 ppm; I is less than 50% mortality when compared to the control; SA is 50%-80% mortality when compared to the control; A is 80%-100% mortality when compared to the control
*Compound 396 provided 100% mortality during the 7-day period

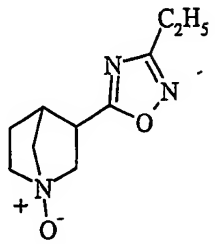
The N-oxides and their corresponding free amines that were tested are set forth below:



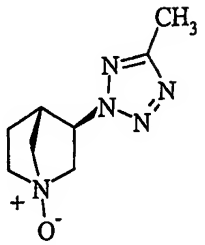
6



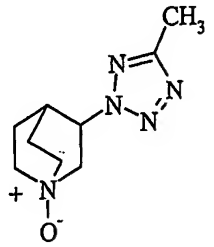
396



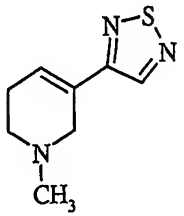
397



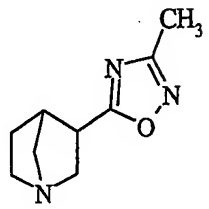
402



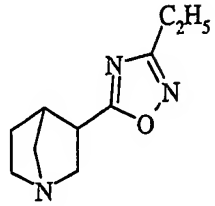
407



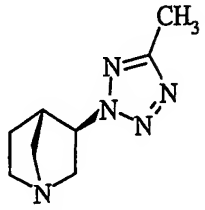
A



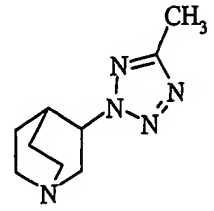
B



C



D



E

As taught in Table 2, above the N-oxide derivatives of the present invention exhibit improved insecticidal activity against cotton aphid when compared to their free amine analogs. The improved insecticidal activity is believed to be the result of the unexpected translaminar properties attributed to the N-oxides. For example, Compound 396 provided 100% mortality throughout the seven-day test period. In contrast, its free amine derivative, Compound B, provided less than 50% mortality of cotton aphid.

Certain N-Substituted azacyclic compounds where the N-substituent is O^- (the N-oxides) of the present invention were also tested to determine their residual insecticidal activity. These tests were conducted in the following manner:

For each rate of application of test compound, a 15 mL aliquot of test solution was prepared. Sufficient test compound was dissolved in 1.5 mL of acetone to provide an application rate as high as 1200 grams/Ha. Each solution was then added to 13.5 mL of water containing 300 ppm of a surfactant. There were four replicates for each rate of application of test compound, and all tests included a known chemical standard as well as a standard of water and untreated checks.

A maximum of 14 appropriately sized cotton plants for each rate of application and replicate were arranged in a 28 pot plastic flat and sprayed with the 15 mL sample of test compound using an traveling boom sprayer equipped with a cone spray tip at a rate of 30 gallons/acre under a pressure of 40-44 psi. The untreated checks were sprayed first, followed by the test compounds and standards, all in order of lowest to highest rates of application. Once the spraying was complete, the test plants were allowed to air-dry on the conveyor on which they were sprayed.

In the test to determine residual activity (0 Day Residual) one set of dry plants was infested with leaf cuttings covered with about 25 cotton aphids taken from cotton plants in an aphid colony. The cotton plants were then maintained in a greenhouse or in an atmosphere of simulated direct sunlight for 72 hours after which time cotton aphid mortality was determined.

A second set of dry test plants treated with test compounds were maintained for three days (3 Day Residual), then infested with cotton aphid. The infested plants were maintained and evaluated for cotton aphid mortality after 72 hours as set forth above. Other residual activity periods are optionally evaluated also, for example a 5 day residual.

At the end of the 72 hour exposure period the numbers of live insects were counted a percent mortality of aphids was calculated based on the number of live insects present and the number that were infested onto the plants. The results of these tests are set forth below:

Table 3
Residual Insecticidal Activity of Certain N-Oxide Derivatives on Cotton Aphid

Cmpd. No.	Rate of Appln (g/ha)	Percent Mortality 0 DAT	3 DAT[1]	3 DAT[2]
396	1120	100	100	100
	560	100	100	100
	224	100	98	99
B	1120	100	99	95
	560	100	84	49
	224	100	41	21

[1]Test was maintained in a greenhouse environment
[2]Test was conducted in a simulated sunlight environment

Table 4
Residual Insecticidal Activity of Certain N-Oxide Derivatives on Cotton Aphid

Cmpd. No.	Rate of Appln (g/ha)	Percent Mortality 0 DAT	3 DAT[1]	5 DAT[2]
396	224	100	98	93
	112	100	70	86
	56	100	58	64
402	224	92	92	84
	112	84	84	70
	56	50	50	45

[1]Test was conducted in a simulated sunlight environment
[2]Test was maintained in a greenhouse environment

As indicated by the results in Tables 3 and 4 above, the N-oxide derivatives of the present invention exhibit improved residual insecticidal activity against cotton aphid when compared to their free amine analogs, as a result of the unexpected translaminar properties attributed to the N-oxides. For example, in Table 3, Compound 396 provided 99% mortality in cotton aphid at a rate of application of 224 g/ha when the test plants were infested with the aphid at 3 days post-treatment. In contrast the corresponding free amine, Compound B, provided only 21% mortality at the same rate of application and time interval. In Table 4, Compound

396, as well as Compound 402, continue to provide unexpected residual insecticidal activity at the lower rates of application of 112 g/ha and 56 g/ha and a longer residual interval of 5 days.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope of the invention as defined by the following claims.